

SEQUENTIAL MEASUREMENTS OF SOIL $\text{NH}_4\text{-N}$ AND $\text{NO}_3\text{-N}$ FROM
TWO-LONG TERM FERTILITY EXPERIMENTS WITH
VARIABLE N RATES, AND DISTRIBUTION OF
SOIL PROFILE $\text{NO}_3\text{-N}$ UNDER FLOODED
CONDITIONS USING A
BROMIDE TRACER

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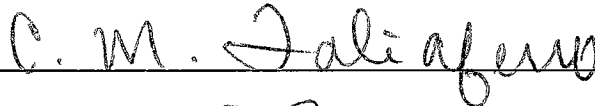
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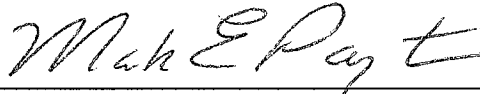
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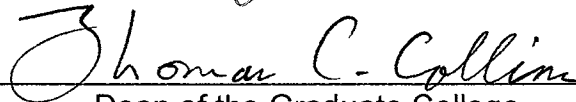


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INTRODUCTION

This dissertation consists of two chapters, each summarizing research problems conducted separately. The chapters are presented in formats suitable for publication in professional journals.

CHAPTER I

SEQUENTIAL MEASUREMENTS OF SOIL $\text{NH}_4\text{-N}$ AND $\text{NO}_3\text{-N}$ FROM TWO LONG-TERM FERTILITY EXPERIMENTS WITH VARIABLE N RATES

ABSTRACT

Several nitrogen indices have been studied that quantify the availability of soil nitrogen to crops. The most accepted have been those that estimate the common forms of N utilized by plants, NH_4^+ and NO_3^- . In Oklahoma $\text{NO}_3\text{-N}$ analysis is used to make N fertilizer recommendations in winter wheat. However, there is little information where both, NH_4^+ and NO_3^- in the soil have been considered simultaneously for improving N recommendations. In addition, soil sampling dates for both NH_4^+ and NO_3^- has not been comprehensively evaluated. Based on that, two long term fertility experiments, 222 and 502 in Stillwater and Lahoma, Oklahoma, respectively, were used to evaluate the relationship of soil NH_4^+ and NO_3^- with grain yield as a function of soil sampling date. Preplant N rate treatments were sampled in experiment 222 (0, 45, 90 and 135 kg N ha⁻¹) and experiment 502 (0, 22.5, 45, 67, 90, and 112 kg N ha⁻¹) at various times over a 3 year period. Fertilizer sources used for N, P, and K were

ammonium nitrate (34-0-0), triple superphosphate (0-20-0) and potassium chloride (0-0-50), respectively. Sixteen cores were taken in each plot at each sampling date, to a depth of 15 cm and analyzed for $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ using an automated injection flow analyzer. In general the use of $\text{NO}_3\text{-N}$ was a better predictor of yield than $\text{NH}_4\text{-N}$, irrespective of date of sampling. Correlation of soil $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ with yield was improved when sampled in the winter. This finding is important considering the potential for topdress fertilization in areas where preplant N was not applied. Because correlation was markedly improved from winter soil sampling, producers may benefit by delaying N fertilization, especially when wheat is produced only for grain.

INTRODUCTION

Accurate prediction of fertilizer needs will become increasingly important in order to improve fertilizer use efficiency. These predictions have been based on a soil test of available nitrogen which gives an idea of how much a farmer will need to apply for a subsequent crop. In other words, nitrogen extracted is correlated with the capacity of a certain soil to supply nitrogen. However, crop response is dependent not only on the fertilizer rate recommended but also on climatic factors. Several nitrogen indices have been studied that quantify the availability of soil nitrogen to crops. The most accepted indices have been those that estimate the common forms of N utilized by plants, NH_4^+ and NO_3^- . In

Oklahoma, $\text{NO}_3\text{-N}$ analysis is used to make N fertilizer recommendations in winter wheat. According to Johnson (1982) the best periods for soil sampling in Oklahoma are before the first tillage operation (June) or just prior to wheat planting (September). Nitrate content of the soil for the sampling dates mentioned has shown that up to 20-30 pounds per acre of N can be subtracted from the fertilizer recommendation when soils are analyzed for $\text{NO}_3\text{-N}$. Samples taken after the first tillage and during mid summer may underestimate available soil N (Johnson, 1982). Although, $\text{NO}_3\text{-N}$ is the most common form of available N, ammoniacal N forms that are products of mineralization have also been studied as indices of N availability (Cornfield, 1960, and Stanford and Smith, 1976).

Forms of nitrogen utilized by plants.

The common forms of N utilized by plants are the inorganic forms NH_4^+ and NO_3^- . Both can be produced during the mineralization process of organic materials in the soil or added to soil as inorganic N fertilizer. According to Stanford and Epstein (1974), the limiting step in mineralization is the conversion of organic N to $\text{NH}_4\text{-N}$, whenever conditions like good soil aeration, and adequate soil moisture occur. Ammonium-N in the soil is oxidized to $\text{NO}_3\text{-N}$ over a broad range of temperatures in such a way that $\text{NH}_4\text{-N}$ generally does not accumulate. Therefore, the rate of $\text{NO}_3\text{-N}$ accumulation can be a good indicator of the rate of soil mineralization (Stanford and Epstein, 1974). Consequently, the

quantities of NH_4^+ and NO_3^- that plants can use depend largely on the amounts applied as N fertilizers and that from the soil organic N pool (Tisdale et al., 1993). The preference of plants for either N form depends on the age and type of plant, the environment and other factors (Tisdale et al., 1993). Assimilation of NH_4^+ can be more efficient when taken up later and converted rapidly to glutamine (Olsen, 1986). Conversely NO_3^- must be transported to the leaves to be reduced (Olsen, 1986).

Factors affecting the availability of mineral nitrogen.

Nitrogen mineralization is described by Tisdale et al., (1993), as the transformation of organic N to NH_4^+ and N immobilization as the reverse, and each process will depend on the C:N ratio of the organic matter being decomposed by soil microorganisms. Results have demonstrated that decomposition of agricultural crop residues with 40% carbon and 1.6% nitrogen (C:N ratio, 25:1) will usually result in immobilization (Paul and Clark, 1989). The importance of soil texture, soil moisture and organic matter in the nitrogen mineralization process has been established under laboratory conditions (Herlihy, 1979). The main factors that limit nitrification in soil are substrate NH_4^+ , O_2 , CO_2 , pH and temperature (Schmidt, 1982). Soil N mineralization is strongly influenced by temperature within the range normally encountered under field conditions (Stanford, et al. 1973). The temperature of greatest interest in soil

biology is generally between 0 and 35°C, because above 35°C ammonification continues, but nitrification essentially ceases at 45° (Stanford et al., 1973). Influence of temperature on nitrification was studied by Sabey et al., (1956) and they found that nitrification decreased with declining soil temperature. Complete inhibition was not observed until soil temperatures approached the freezing point. The optimal temperature for nitrification in pure culture ranges from 25-35°C (Focht and Verstraete, 1977). According to Alexander, (1977), temperature affects the mineralization sequence as each biochemical step is catalyzed by a temperature-sensitive enzyme produced by microorganisms whose growth is in turn conditioned by temperature. Therefore, at 2°C, the microflora slowly mineralizes organic complexes but there is no increase in ammonium or nitrate when soil is frozen. In opposition to most microbiological transformations, the optimum temperature for ammonification is not in the mesophylic range but rather it is above 40°C, and usually between 40 and 60°C (Alexander, 1977). Nitrogen and carbon mineralization as affected by drying and rewetting was studied by Agarwal, et al. (1971), and they observed that drying temperature as well as drying-rewetting cycles enhanced N and C mineralization in practically all soils. They also mentioned that there was generally greater N release when incubation after drying was included than when omitted. Wetting and drying cycles in soil have a pronounced effect upon all microbial processes, presumably due to the physical breaking of bonds to liberate smaller, more labile organic molecules (Focht and Verstraete, 1977). According to Birch (1958), low rainfall

(non-humid periods between rain) in Kenya in contrast with high rainfall will be associated with a greater frequency of the drying and wetting cycle and therefore greater nitrate production. Birch (1958) also indicated that any practice that intensifies soil drying should lead to more nitrate production when the rains begin. Lund and Goksoyr (1980), said that after drying and rewetting periods in the soil the overall effect is an increase in the mineralization rate where easily available nutrients from dead organisms are used first and ending with mineralization of humic substances. While studying the effect of soil moisture stress on uptake and recovery of tagged nitrogen by wheat, Paul and Myers (1971) observed that immobilization of N was highest at low moisture stress where plant growth was the greatest but that mineralization was unaffected by moisture stress. The same authors found that losses of N were greater in soils exposed to high moisture stress and were related to the residual $\text{NO}_3\text{-N}$ in the soil. It is reported that aerobic microbial activity is favored by water content up to a point where diffusion and availability of oxygen is affected (Linn and Doran, 1984). Campbell et al. (1981) indicated that the nitrogen supplying power of the soil depends on mineralizable organic nitrogen, the mineralization rate, moisture and temperature. Most microbial respiration is independent of oxygen concentrations. However, Michaelis constant (K_m), for oxygen consumption by *Nitrosomonas* and *Nitrobacter* is significantly higher, ranging from 0.3 to 1.0 mg O_2/lt (Focht and Verstraete, 1977). The higher respiratory K_m of the autotrophic nitrifiers vs. heterotrophic bacteria means that the former would be poorer

competitors for oxygen at lower concentrations. Therefore, heterotrophic respiration would be increased with a possible reduction of soluble oxygen upon the addition of an available source of carbon (Focht and Verstraete, 1977).

Soil nitrogen tests as indicators of soil nitrogen availability

Accurate and precise soil mineral N analyses continue to be important in research projects where N indices are developed. The estimation of soil N has changed with time as various incubation methods (biological tests) and chemical tests have been proposed. For example, Cornfield (1960) indicated that the most reliable method for establishing nitrogen availability indices was the incubation procedure, where soils are incubated under optimum conditions of temperature and moisture for a certain period of time and the amount of nitrogen mineralized determined. Searching for a method of routine soil analysis Waring and Bremmer (1964), found a close relationship between the amount of $\text{NH}_4\text{-N}$ produced by using a method of incubating the soil under waterlogged conditions. Among the advantages that they claimed for their method when compared to other incubation methods were that their method was rapid (less than 2 weeks), precise, applicable to both air dried and field moist soils, did not require corrections and only ammonium produced needed to be determined. Keeney and Bremmer (1966) compared the procedure of Waring and Bremmer (1964) and a newer modification to four other chemical methods using 25 Iowa soils.

They found that incubation results were affected by air drying the sample and air-dry storage, conversely, chemical methods were not affected and therefore provided good indices of nitrogen availability. Fox and Pikielak, (1978) found that absorbance of a 0.01M NaHCO₃ soil extract at 260 nm was correlated (r = 0.865 P<0.01) with N supplying power of the soil. Nitrogen availability indices do not include existing inorganic N when the sample was taken, because they are a measure of the potential of a soil to supply N (Dahnke and Johnson, 1990). In recent times residual NO₃-N tests have proven to be reliable (Dahnke and Johnson, 1990). Dahnke and Johnson, (1990) further noted that NH₄-N has limited use in testing for residual inorganic N.

Determination of inorganic nitrogen in soils

According to Bremmer (1965a) the main idea of an appropriate time of sampling is to take the soil sample close to the cropping period and under a stable climatic regime. However, in climates where there is a defined dry season preceding the rainy crop season, it is often the practice to take samples just prior to the expected onset of the first rains (Saunders, Ellis and Hall, 1957). Dahnke and Johnson (1990), stated that the time of sampling depends on climate. When considering the window for soil sampling wheat fields in Oklahoma (June-September), Johnson (1982), noted that the ideal times were either before the first tillage operation or near the end of summer.

Soil sampling is accomplished for practical reasons to a predetermined uniform depth in the immediate topsoil layer (0-20 cm), generally the richest in organic matter and total nitrogen (Robinson, 1979). It has been observed that sequential deep soil samples commonly show a decrease in potentially mineralizable-N, correlating less with crop parameters when compared to mineral nitrogen in the top soil (Robinson, 1979). However, for some crops and under certain conditions, deep mineral-nitrogen has been found to be important. For example, when sampling for residual $\text{NO}_3\text{-N}$, samples are generally taken to a depth of 60 cm (Dahnke and Johnson, 1990).

Soil inorganic nitrogen status

Determination of NH_4^+ , NO_3^- , and NO_2^- in soils is not easy due to the rapid biological transformations that can occur in the sample, consequently changing the forms of inorganic N in the sample (Keeney and Nelson, 1982). Robinson (1979), stated that when measuring soil mineral nitrogen status in the laboratory, mineralizable-N is the sum of that determined in the original fresh sample, plus any acquired in transit to the laboratory and additions due to laboratory preparation and storage. Deep-freezing and drying at laboratory temperatures can be used as preservation methods, and there are reports that no marked changes have been found in inorganic N content of soils stored one year after drying was performed (Keeney and Nelson, 1982).

However, there is little information where both, $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ in the soil have been considered simultaneously for improving N recommendations indices. In addition soil sampling date for both $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ has not been comprehensively evaluated. Therefore, the objectives of this study were to evaluate seasonal changes in soil $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ in two long-term fertility experiments and their relationship with time, measured climatic variables and grain yield.

MATERIALS AND METHODS

Two long-term fertility experiments were selected that had received annual rates of applied N for over 20 years in continuous winter wheat. The experimental sites included experiment 222 (initiated in 1969) located at the Agronomy Research Station in Stillwater, OK and experiment 502 (initiated in 1971) on the North Central Research Station near Lahoma, OK. The soil at Stillwater is a Kirkland silt loam (fine, mixed, thermic, Udertic Paleustoll) and at Lahoma a Grant silt loam (fine-silty, mixed, thermic, Udic Argiustoll). Initial soil test characteristics at each location are reported in Table 1. Mean annual rainfall over the time periods for which these studies have been conducted was 922 and 765 mm at Stillwater and Lahoma respectively. The experimental design at both sites was a randomized complete block with four replications. Plot size in these continuing experiments is 6.09 x 18.3 m in experiment 222, and 5.0 x 18.3 m in

experiment 502. Plots containing four treatments were sampled in experiment 222 and six in experiment 502 (Table 2). Soil sampling and plot management dates by year and location are reported in Table 3. Fertilizer sources used for N, P, and K were ammonium nitrate (34-0-0), triple superphosphate (0-20-0) and potassium chloride (0-0-50), respectively. Sixteen cores were taken in each plot at each sampling date, to a depth of 15 cm. Samples were dried at ambient temperature and ground to pass a 20 mesh screen. A subsample of 2 grams was then extracted with 2M KCl (Keeney and Bremner, 1966), and extracts were analyzed for $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ using an automated injection flow analyzer. In addition to surface samples, soil cores were taken to a depth of 1.22 m to evaluate residual $\text{NO}_3\text{-N}$ in the soil profile; however, these results are not discussed in this report. Daily temperature and precipitation were recorded at both locations. Analyses of variance for soil $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ at each of the sampling dates was performed at both locations. The standard error of the difference (SED) between two equally replicated means was determined by date. Linear and quadratic single-degree-of-freedom contrasts were also evaluated. Since samples were taken over an entire range of dates, analyses were accomplished considering crop year independently.

RESULTS AND DISCUSSION

In general, the Lahoma experiment has been conducted on a soil that has better drainage than the soil at Stillwater. Both soils fall within the 'thermic' temperature regime, having a mean soil annual temperature of 15°C or higher, but lower than 22°C (Soil Conservation Service, 1975).

Stillwater, OK, Experiment 222, crop year 1991-92

A significant linear response of $\text{NH}_4\text{-N}$ to N fertilization was found at all dates excluding September 9 and March 13 (Table 4 and Figure 1). Air temperature maximums and precipitation for this same time period are plotted accordingly in Figure 1. Surface soil $\text{NH}_4\text{-N}$ in the first sampling date (one day prior to fertilization) was found to be significantly affected by N rate (Table 4, 0.10 probability level). Following fertilization (9/10/91) surface soil $\text{NH}_4\text{-N}$ showed corresponding increases with N rates and time up to 63 days (Figure 1). However, surface soil $\text{NH}_4\text{-N}$ in the check plot (0N) did not increase with time. A tendency for small decreases was noted for $\text{NH}_4\text{-N}$, 63 to 134 days after fertilizers were applied. With the increased temperature and cumulative precipitation received (134 to 186 days after fertilizers were applied), a marked increase in $\text{NH}_4\text{-N}$ was noted for the March 13 sampling date (Figure 1). Crop uptake and accumulation of $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ in vegetative tissue is known to be taking place during this

time (Gardner and Jackson, 1976, Raun and Westerman, 1991). However, even with the crop variable included, the significant increase in $\text{NH}_4\text{-N}$ 134 to 186 days after fertilizers were applied suggests that ammonification was taking place. A different tendency was observed from 186 to 239 days following fertilization as a sharp decrease in $\text{NH}_4\text{-N}$ with no comparative change in $\text{NO}_3\text{-N}$ was characteristic of immobilization.

Similar to results for $\text{NH}_4\text{-N}$ noted at this location, a significant linear response to N fertilization was found for $\text{NO}_3\text{-N}$ at all dates excluding September 9 and March 13 (Table 4 and Figure 1). Twenty five days after fertilizers were applied, $\text{NO}_3\text{-N}$ levels increased significantly and then declined at the 35 and 63 day sampling dates for all treatments. Given that these plots are representative of long-term applications, it was interesting to observe an increase (0-35 days) in $\text{NO}_3\text{-N}$ in the check plot where no fertilizers have been applied for over 20 years. This suggests that fluctuations in mineral-N as a function of the total organic-N pool were still notable in plots receiving no N for over twenty years. Because temperature and precipitation were favorable for mineralization and more specifically, nitrification, between the first and second sampling date, an increase in both $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ was expected since N applications would narrow the C:N ratio. This was also noted, however, in the check plot receiving no N fertilization. Nitrate-N subsequently increased between the 63 and 87 day sampling dates in all plots receiving N. This increase was associated with a corresponding decrease in $\text{NH}_4\text{-N}$ at the same respective dates. Given the

abnormally low (late October) followed by abnormally high ambient temperatures (mid November) in association with above average precipitation received during this time period (Figure 1), it is thought that nitrification was taking place. The markedly low temperatures noted at the beginning of November (-5 to 10°C) may have affected microbial oxidation of $\text{NH}_4^+\text{-N}$ to $\text{NO}_3^-\text{-N}$. According to Brady (1990), this process proceeds rapidly at soil temperatures of 27 to 32°C and is negligible below 10°C. Between the fourth and sixth sampling (63 to 134 days after fertilization), the mild temperature conditions (13 to 23°C) associated with short wetting (precipitation) and drying periods (precipitation) may have favored the nitrification process. Work by Lund and Goksoyr, (1980) has indicated that fluctuating water activity in the soil can result in more rapid decomposition and mineralization of the microbial biomass. Only very small changes in surface soil $\text{NO}_3\text{-N}$ were noted during the 134 to 186 day period (Figure 1). The nitrification rate may have been slower than that mentioned for ammonification; however, because $\text{NO}_3\text{-N}$ is mobile and is known to accumulate in wheat during this time period (134 to 186 days), it was not surprising to find small differences in this soil test variable. By the May sampling date, 239 days following fertilization, surface soil $\text{NO}_3\text{-N}$ levels were all less than 10 mg kg^{-1} , which was very similar to that noted when sampling was initiated. Because surface soil $\text{NO}_3\text{-N}$ would be subject to crop depletion, leaching, and possible immobilization and/or denitrification during the 239 day period, only limited amounts were expected in these surface samples following the given time period.

Stillwater, OK, Experiment 222, crop year 1992-93

The 1992-93 crop year included six sampling dates. A linear response of surface soil $\text{NH}_4\text{-N}$ to N fertilizer rates was significant at all times excluding June 17 and August 3, 1993, (Figure 2 and Table 5). Similarly, a significant linear response of surface $\text{NO}_3\text{-N}$ to N fertilization was found at sampling dates later in the season. Ammonium levels for the first three sampling dates were all under 10 mg kg^{-1} (Figure 2) and similar to that reported for the last sampling date of the 1991-92 crop year (May 5, 1992). These three dates encompassed a period of 89, 43 and 6 days before fertilizer application. Because only minor differences were observed in $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ prior to fertilization, preplant soil test analysis did not detect larger inorganic N pool differences. Both $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ increased following fertilization (Figure 2 and Table 5) and then sharply decreased (174 days after fertilizer application). The peak in $\text{NH}_4\text{-N}$ in December of 1992 was similar to that found for $\text{NO}_3\text{-N}$. These results were somewhat different to that noted in 1991 where $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ levels did not parallel each other. Similar to the 1991-1992 crop year, 250 days after the fertilizers were applied soil $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ showed limited differences as a function of N applied. According to Focht and Verstraete (1977) it has been well established that, upon thawing of frozen soils, organic matter is readily mineralized. This may have happened with this experiment considering the above normal temperatures found prior to the December 31, 1992 sampling

date. When studying the influence of temperature on nitrification under laboratory and field conditions, Sabey et al. (1956) found that nitrification was more rapid under field conditions when compared to laboratory conditions at temperatures below 8°C and attributed this phenomena to diurnal fluctuations in temperature, as complete inhibition was not attained until soil temperatures approached the freezing point. Frederick (1956), while studying the formation of nitrate from ammonium nitrogen in several soils, observed that the rate of nitrification had the greatest change occurring between 7 and 15 °C. He considered that an application of 50 pounds per acre of ammonium nitrogen in some soils, could be nitrified in about 2 months even when the average temperature is near freezing (0 to 2° C).

By March 10, 1992, soil NH₄-N and NO₃-N had decreased to sub 10 mg g⁻¹ levels. Similar to the 1991-1992 crop year, 250 days after the fertilizers were applied, soil NH₄-N and NO₃-N showed limited differences as a function of N applied.

Stillwater, OK, Experiment 222, crop year 1993-94

Four sampling dates are included for this period. A significant linear response to NH₄-N was found only for one sampling date (May 13, 1994, Table 6). Considering that fertilization for this crop year was on September 22, 1993, values of NH₄-N for the first sampling date, July 8 (27 to 35 kg⁻¹) were unusually

high when compared to similar dates in 1991 and 1992 (Figures 1 and 2). Conversely, soil $\text{NO}_3\text{-N}$ levels for the same sampling date were low (less than 5 mg kg^{-1}) and similar to others reported for similar dates in this study. The unusually high levels of $\text{NH}_4\text{-N}$ and the low levels of $\text{NO}_3\text{-N}$ obtained for the sampling date on July 8 (Figure 3) are hard to explain, especially for a period when immobilization is expected. During the inter-sampling period of 36 days between June 3 and July 8 of 1993, an average temperature of 25°C was observed and a total of 6.8 cm of intermittent rain was received. These conditions were considered ideal for mid-summer nitrification. Therefore, it may be assumed that other factors are affecting the nitrifying populations and consequently the nitrification process. For example, heterotrophic respiration may have been increased upon the addition of wheat crop residues reducing the availability of soluble oxygen when concentrations of oxygen in the soil are lower.

High soil $\text{NH}_4\text{-N}$ ($23\text{-}28 \text{ mg kg}^{-1}$) and low $\text{NO}_3\text{-N}$ observed on September 21 are also difficult to explain. This would suggest that a net N immobilization continued to take place since an NH_4NO_3 source was added. Because plant preference for $\text{NO}_3\text{-N}$ was not expected during this time, it is not understood why soil $\text{NO}_3\text{-N}$ was low.

Soil $\text{NH}_4\text{-N}$ levels for the third sampling date on March 16, 1994 (174 days after fertilizers were applied), were similar (Figures 1, 2 and 3) to that found in 1992 and 1993. Soil $\text{NO}_3\text{-N}$ levels were also low and corresponded to levels

detected around the same dates in 1992 and 1993. The final sampling date on May 13, 1994 was found to be significantly affected by N rate (Table 6 and Figure 3), however, values of both ions were low and similar to the ones found on May 2, 1992. Soil mineral nitrogen is usually depleted by May in continuous winter wheat production systems.

Lahoma, OK, Experiment 502 crop year, 1991-92

In Experiment 502 near Lahoma, OK, analyses of variance for surface soil $\text{NH}_4\text{-N}$ indicated that the main effect of N-rate was significant in eight of the ten sampling dates (Table 7). Partitioning the main effect of N rate into orthogonal linear and quadratic single degree of freedom contrasts demonstrated that surface soil $\text{NH}_4\text{-N}$ was detectable as a linear function of N rate at all sampling dates excluding August 28 before fertilizers were applied. Following fertilization, $\text{NH}_4\text{-N}$ was significantly affected by N rate up to 196 days after fertilization. Surface soil $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ are represented as a function of time and N rate in Figure 4. Unlike results noted at the Stillwater location, $\text{NH}_4\text{-N}$ levels were below 10 mg kg^{-1} by 88 days after fertilizers were applied. However, as expected, and similar to that noted at the Stillwater location, $\text{NH}_4\text{-N}$ showed positive linear correlation with N rate immediately following fertilization. Only limited fluctuations in $\text{NH}_4\text{-N}$ were observed 11 to 76 days after fertilizers were applied. From 76 to 88 days after fertilizers were applied, a sharp decrease in $\text{NH}_4\text{-N}$ was noted with a

corresponding tendency for increased surface soil $\text{NO}_3\text{-N}$. By the last three sampling dates, 141, 196 and 243 days after fertilization, $\text{NH}_4\text{-N}$ levels had declined significantly. It is important to note that even within this extremely small range ($0\text{-}10 \text{ mg kg}^{-1} \text{ NH}_4^+\text{-N}$), a significant linear relationship was detected for N rate 88, 141 and 196 days after fertilization. This would appear to indicate that the combined experimental precision (random error) and associated laboratory accuracy (bias error) was extremely sensitive. Because this was also noted at the Stillwater location, it would further suggest that the experimental precision needed to estimate $\text{NH}_4\text{-N}$ (given the procedures employed) within a long-term experiment, is more than adequate. If $\text{NH}_4\text{-N}$ were to be used as a soil test index variable for improving N recommendations, present laboratory, sampling and field experimental procedures appear to be minimizing random and bias errors since the controlled independent variable (N rate) was highly significant.

Surface soil $\text{NO}_3\text{-N}$ from the ten Lahoma sampling dates demonstrated linear increases with N rate both before fertilization and up to 196 days following the time when fertilizers were applied (significant N-Rate linear, Table 7). It was interesting to note a significant relationship between soil $\text{NO}_3\text{-N}$ and N rate (August 28, 1991 before fertilizers were applied in 1991) more than 1 year after fertilizers were applied in 1990 (August 2, 1990). However, prior to fertilization, only the 90 and 112 kg N ha^{-1} rates were significantly greater than the check indicating that residual amounts (following harvest, 8/28/91) in the soil were minimal for the 22.5, 45, and 67 kg N ha^{-1} rates (Table 7 and Figure 4). The marked decrease in soil

NO₃-N 36 to 42 days after fertilization is difficult to explain. During this time period, soils at this site were initially very wet and then subjected to abnormally high temperatures for over 20 days (Figure 4). Marginal decreases were then noted up until the last two sampling dates 196, and 243, days after fertilization, where small increases in NO₃-N were found (Figure 4). Surface soil NO₃-N found in the 141, 196 and 243 day sampling dates was below that measured before fertilization when sampling was initiated (Figure 4).

Lahoma, OK, Experiment 502, crop year 1992-93

Four sampling dates showed a significant linear response of NH₄-N to N rate (Table 8). Similar values of NH₄-N and NO₃-N were found for the June 18 sampling date as both were extremely low. However an increase in NH₄-N values (20-30 mg kg⁻¹) were observed for the next sampling date on July 22, 25 days before fertilizers were applied. Corresponding levels of soil NO₃-N for the same date were low and less than 5 mg kg⁻¹. Harvest for the Lahoma experiment in 1992 was late (June 16). By July 22 wheat straw residues had sufficient time to decompose, since incorporation took place immediately following harvest. Given the abnormally high rainfall from June 16 to July 22 and the high summer temperatures, NH₄-N was a direct product of the ideal conditions for mineralization. It is, however, not understood why NO₃-N was not detected, since the biological transformations of NH₄-N to NO₃-N is known to be rapid. Factors like restriction of

oxygen diffusion rates when available carbon is high may help to explain a possible reduction of nitrate when oxygen is limiting and heterotrophic respiration is high.

Forty-two days after fertilizers were applied, soil $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ levels remained high. Soil $\text{NH}_4\text{-N}$ levels remained high 97 days after fertilizers were applied while $\text{NO}_3\text{-N}$ levels decreased significantly (Table 8 and figure 5). By March 9, 1993, similar $\text{NO}_3\text{-N}$ levels remain in the soil, similar to that observed for March 12, 1992.

Lahoma, OK, Experiment 502, crop year 1993-94

At three of the four sampling dates, soil $\text{NH}_4\text{-N}$ showed a significant response to preplant N. Alternatively, soil $\text{NO}_3\text{-N}$ appeared to be an excellent indicator of preplant N rate in this long term experiment since this relationship was significant on all but one date (Table 9). Soil $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ levels were low for the first three sampling dates as all were below 15 mg kg^{-1} . Average temperatures for this period were in the upper twenties and precipitation occurred regularly (Figure 6). A small increase in soil $\text{NH}_4\text{-N}$ was observed by the third sampling date on August 19, 1993 just before fertilization. It was interesting to find that soil $\text{NH}_4\text{-N}$ levels remained high and significantly correlated with N rate 118 days after fertilizers were applied. Soil $\text{NH}_4\text{-N}$ declined to $<.10 \text{ mg kg}^{-1}$ by the last two sampling dates.

Similar to observations made for $\text{NH}_4\text{-N}$, it was remarkable to still find soil $\text{NO}_3\text{-N}$ 110 days after fertilizers were applied (Figure 6). Data presented in Figure 6 on temperature and rainfall showed that temperatures oscillated from $-6\text{ }^\circ\text{C}$ to $11\text{ }^\circ\text{C}$ and a dry period was predominant before the January 11 sampling. As was discussed earlier, nitrification has been reported to occur at low temperatures (Frederick, 1956). Campbell et al. (1971), found that ammonium concentrations in sterile soils that were conditioned to fluctuating temperatures were higher than in soils held at fixed mean temperatures. Nitrate levels for the two final sampling dates decreased according to similar findings for comparable dates in 1992 and 1993. Values of both ions for the last sampling date on May 17, of 1994 were low and appropriate for a pre-harvest period in which depletion of inorganic nitrogen in the soil occurred.

Regression analyses

In general, soil $\text{NO}_3\text{-N}$ analysis from fall and winter samplings were highly correlated with wheat grain yield (Tables 10 and 11) at both locations. This suggests that topdress N application strategies could incorporate soil $\text{NO}_3\text{-N}$ or a possible plant parameter to reliably adjust N rates on winter months. Prediction of grain yield using soil $\text{NH}_4\text{-N}$ produced variable results, however this analyses remained significant in winter months.

CONCLUSIONS

Sequential surface soil samples (0-15 cm) were taken during the months of August, 1991 through May, 1992 from two long-term soil fertility experiments with variable N rates (Experiment 222, Stillwater, OK and Experiment 502, Lahoma, OK). Samples were analyzed for $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ as defined by Keeney and Bremner, 1966. In general, it was difficult to detect differences in surface soil $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ prior to the time when fertilizers were applied (September). Soil $\text{NO}_3\text{-N}$ analysis collected in winter months was found to be a reliable predictor of grain yield. Results from this study suggest that $\text{NH}_4\text{-N}$ may need to be included within the soil N test which at present establishes N recommendations based only on $\text{NO}_3\text{-N}$. Because yield prediction based on ammonium and nitrate was significant for winter soil samplings when temperatures are low and no nitrification is expected, topdress applied N recommendations could easily utilize this sampling technology.

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Table 1. Initial surface (0-15 cm) soil test characteristics from check plots at experimental sites.

Location	pH	P, mg kg ⁻¹	K, mg kg ⁻¹	BI
Stillwater, OK., Experiment 222	5.0	61	366	6.7
Lahoma, OK., Experiment 502	5.3	146	822	6.7

pH-1:1 soil:water, P and K - Mehlich III

Table 2. Treatments selected at each location, and corresponding rates of N,P,K applied annually at planting.

Treatments	N	P	K
		-----kg ha ⁻¹ -----	
Stillwater, Experiment 222			
1	0	29	38
2	45	29	38
3	90	29	38
4	135	29	38
Lahoma, Experiment 502			
2	0	20	56
3	22.5	20	56
4	45	20	56
5	67	20	56
6	90	20	56
7	112	20	56

Table 3. Fertilization, harvest, planting and soil sampling dates for experiments 222, Stillwater, OK and 502, Lahoma, OK, 1991-1994.

Activities	1991-1992		1992-1993		1993-1994	
	Stillwater 222	Lahoma 502	Stillwater 222	Lahoma 502	Stillwater 222	Lahoma 502
Soil sample	9/9/91	8/28/91	6/17/92, 8/3/92, 9/10/92	6/18/92, 7/22/92	7/8/93, 9/21/93	6/17/93, 7/19/93 8/19/93
Fertilization	9/10/91	8/29/91	9/16/92	8/17/92	9/22/93	9/13/93
Soil sample		9/9/91, 9/23/91		9/29/92		
Planting	9/30/91	9/26/91	10/12/92	10/1/92	9/27/93	9/28/93
Soil sample	10/4/91, 10/14/91	10/4/91, 10/10/91	12/3/92, 3/10/93	12/2/92	3/16/94, 5/13/94	1/11/94, 3/17/94
Soil sample	11/11/91, 12/5/91	11/13/91, 11/25/91	6/3/93	3/9/93		5/17/94
Soil sample	1/21/92, 3/13/92	1/17/92, 3/12/92				
Soil sample	5/2/92	4/29/92				
Harvest	6/17/92	6/16/92	6/17/93	6/16/93		

Table 4. Analyses of variance for soil NH₄-N and NO₃-N (0-15 cm), from eight sampling dates in experiment 222, Stillwater, OK., 1991-1992.

Days after fertilization		-1	25	35	63	87	134	186	239
Dates		9/9/91	10/4/91	10/14/91	11/11/91	12/5/91	1/21/92	3/13/92	5/2/92
Source of variation	df			Mean	squares	NH ₄ -N			
Rep	3	18.50	98.75	49.54	80.11	49.91	3.60	15.71	13.70
Trt	3	15.36	276.05**	527.85	1166.85*	114.39**	121.85**	118.16	29.54
Error	9	10.95	36.78	157.24	54.84	56.82	8.30	86.37	10.93
SED		5.47	18.39	78.62	27.42	28.41	4.15	43.36	5.46
N-rate linear	1		**	*	**	**	**		*
N-rate quadratic	1	@				*	*		
Coefficient of variation, %		32	38	62	35	45	38	41	79
Source of variation	df			Mean	squares	NO ₃ -N			
Rep	3	5.54	138.61	4.55	6.48	8.64	3.28	1.97	1.08
Trt	3	5.35	614.26*	104.02	71.08**	410.66**	106.90**	7.15	3.82*
Error		15.39	114.15	36.47	2.80	6.06	2.19	2.84	0.92
SED		7.7	57.07	18.23					
N-rate linear	1		**	*	**	**	**		*
N-rate quadratic	1				**				
Coefficient of variation, %		44	34	39	17	15	23	26	20

@, *, ** - significant at the 0.10, 0.05 and 0.01 probability levels, respectively.

Table 5. Analyses of variance for soil NH₄-N and NO₃-N (0-15 cm), from six sampling dates, experiment 222, Stillwater, OK, 1992-1993

Days after fertilization		-89	-43	-6	77	174	257
Dates		6/17/92	8/3/92	9/10/92	12/3/92	3/10/93	6/3/93
Source of Variation	df		Mean	Squares	NH ₄ -N		
Rep	3	7.15 *	3.95	1.33*	6.36	1.66	1.80
Trt.	3	1.07	1.51	4.99**	117.39**	130	20.65 **
Error	9	1.26	3.82	1.54	7.26	2.99	1.77
SED		0.63	1.91	0.77	3.63	1.495	0.88
N rate linear				*	**	**	**
N rate quadratic				@	*	**	@
Coefficient of variation		19.93	22.07	14.43	17.40	13.56	11.66
Source of Variation	df		Mean	Squares	NO ₃ -N		
Rep.	3	0.296	0.0077	0.109	6.17	0.89	0.199
Trt	3	1.53	0.619	0.080	250.71	30.70	0.548
Error	9	0.79	0.295	0.46	11.09	0.93	0.166
SED		0.395	0.1475	0.23	5.54	0.465	0.083
N rate linear				*	**	**	*
N rate quadratic		@			**	**	
Coefficient of variation		18.23	25.95	17.17	28.65	45.48	38.59

@, *, ** - significant at the 0.10, 0.05 and 0.01 probability levels, respectively.

Table 6. Analyses of variance for soil NH₄-N and NO₃-N (0-15 cm), from four sampling dates experiment, Stillwater, OK, 1993-1994.

Days after fertilization		-73	-1	174	231
Dates		7/8/93	9/21/93	3/16/94	5/13/94
Source of variation	df	Mean	squares	NH ₄ -N	
Rep	3	28.18	62.59	12.26	0.75
Trt.	3	66.54	22.02	20.07	8.17**
Error	9	63.84	72.70	20.27	0.67
SED		31.92	36.35	10.13	0.33
N rate linear					**
N rate quadratic					
Coefficient of Variation		25.45	34.03	30.98	19.96
Source of variation	df	Mean	squares	NO ₃ -N	
Rep	3	20.64	2.02	0.009	0.39
Trt	3	11.82	1.56	0.029	0.92
Error	9	3.23	0.85	0.076	0.38
SED		1.61	0.425	0.038	0.19
N rate linear					@
Nrate quadratic					
Coefficient of variation		91.30	43.80	8.94	18.38

@, *, ** - significant at the 0.10, 0.05 and 0.01 probability levels, respectively.

Table 7. Analyses of variance for soil NH₄-N and NO₃-N (0-15 cm), from ten sampling dates in experiment 502, Lahoma, OK, 1991-1992.

Days after fertilization		-1	11	25	36	42	76	88	141	196	243
Dates		8/28/91	9/9/91	9/23/91	10/4/91	10/10/91	11/13/91	11/25/91	1/17/92	3/12/92	4/29/92
Sources of variation	df				Mean	squares	NH ₄ -N				
Rep	3	5.26	93.33	45.61	20.37	4.26	15.68	1.80	2.35	6.53	3.26
Trt	5	4.25	306.04**	234.95**	247.70**	333.52**	48.82**	14.32**	4.79	2.02	
Error	15	2.47	49.83	11	10.77	19.01	12.46	2.61	1.71	2.92	1.82
SED		1.23	24.91	5.5	5.38	9.50	6.23	1.30	0.85	1.46	0.91
N-Rate linear	1		**	**	**	**	**	**	**	*	
N-Rate quadratic	1		**	**	**	**	**	**			
Coefficient of variation		35	40	40	27	33	32	29	29	45	36
Sources of variation	df				Mean	squares	NO ₃ -N				
Rep	3	1.98	25.87	15.55	12.21	4.83	1.83	12.38	0.87*	0.57	1.55@
Trt	5	101.81**	1038.63**	881.51**	1192.48**	169.40**	20.36**	58.23**	7.49**	2.70	0.22
Error	15	13.16	15.81	11.85	31.82	17.85	1.77	13.96	0.25	1.0	0.52
SED		6.58	7.90	5.92	15.91	8.92	0.88	6.98	0.125	0.5	0.26
N-Rate linear	1	**	**	**	**	**	*	**	**	**	
N-Rate quadratic	1								*		
Coefficient of variation		25	12	10	13	26	22	67	21	27	17

@, *, ** - significant at the 0.10, 0.05 and 0.01 probability levels, respectively.

Table 8. Analyses of variance for soil NH₄-N and NO₃-N (0-15 cm), from six sampling dates, in experiment 502, Lahoma, OK, 1992-1993.

Days after fertilization	69	-25	0	42	63	97	
Dates	6/18/92	7/22/92	8/17/92	9/29/92	12/2/92	3/9/93	
Source of variation	df		Mean	squares	NH ₄ -N		
Rep	3	1.01	355.22**	8.77	3.58	48.93*	13.64
Trt	3	1.61	66.62	23.85	128.84**	127.11**	54.42**
Error	9	1.46	31.87	12.46	5.73	10.39	9.75
SED		0.73	15.93	6.23	2.86	5.14	4.875
N rate linear			@		**	**	**
N rate quadratic					**	**	
Coefficient of variation		22.19	22.83	19.61	22.70	28.66	28.07
Source of Variation	df		Mean	squares	NO ₃ -N		
Rep	3	0.38	0.46	1.35	29.48	35.38*	0.23
Trt	3	2.33	0.16	7.77	219.65	28.04*	1.35**
Error	9	1.51	0.48	2.19	5.97	663.80	24.56
SED		0.755	0.24	1.095	2.98	331.9	12.28
N rate linear		*		**	**	**	**
N rate quadratic					*		*
Coefficient of variation		27.27	27.86	26.49	11.16	54.10	24.56

@, *, ** - significant at the 0.10, 0.05 and 0.01 probability levels respectively.

Table 9. Analyses of variance for soil NH₄-N and NO₃-N (0-15 cm), from six sampling dates experiment 502, Lahoma, OK, 1993-1994.

Days after fertilization		-86	-54	-24	118	282	346
Dates		6/17/93	7/19/94	8/19/93	1/11/94	3/17/94	5/17/94
Source of variation	df		Mean	squares	NH ₄ -N		
Reps.	3	1.99	24.00	20.63*	24.26	56.01@	3.05
Trts.	3	5.43	7.96	12.48*	133.89**	55.08*	15.90
Error	9	8.14	17.49	4.14	21.97	12.30	7.57
SED		4.07	8.74	2.07	10.98	6.15	3.78
N rate linear				@	**	*	
Nrate quadratic						**	
Coefficient of variation		28.84	61.95	16.88	15.75	26.93	43.91
Source of variation	df		Mean	squares	NO ₃ -N		
Rep	3	3.01	24.29	11.49	22.30	2.48	0.13
Trt	3	16.02	39.23	47.74	996.65**	21.99**	0.35
Error	9	3.47	8.83	5.91	46.15	1.74	0.21
SED		1.73	4.41	2.95	23.07	0.87	0.10
N rate linear		**	**	**	**	**	
Nrate quadratic			*	@	*	**	
Coefficient of variation		108.02	46.56	53.60	45.03	34	14.31

@, *, ** - significant at the 0.10, 0.05 and 0.01 probability levels respectively.

Table 10. Simple linear regression equations and significance for grain yield on NH₄-N and NO₃-N (0-15 cm), for selected dates, experiment 222, Stillwater, OK.

Date	Model	r ²	Prob>F
5/13/94	Yld = -0.092 + 0.35 NH ₄ -N	0.74	0.0001
12/5/91	Yld = 0.87 + 0.044 NO ₃ -N	0.70	0.0001
11/11/91	Yld = 0.63 + 0.099 NO ₃ -N	0.67	0.0001
6/3/93	Yld = -1.07 + 0.21 NH ₄ -N	0.64	0.0003
3/10/93	Yld = 0.24 + 0.088 NH ₄ -N	0.59	0.0004
1/21/92	Yld = 1.11 + 0.078 NO ₃ -N	0.56	0.0008
12/3/92	Yld = 0.99 + 0.038 NO ₃ -N	0.55	0.0046
3/10/93	Yld = 1.02 + 0.16 NO ₃ -N	0.50	0.0021

@, *, ** - significant at the 0.10, 0.05 and 0.01 probability levels respectively.

Table 11. Simple linear regression equations and significance for grain yield on NH₄-N and NO₃-N (0-15 cm), for selected dates, experiment 502, Lahoma, OK.

Date	Model	r ²	Prob>F
1/11/94	Yld = 1.08 + 0.005 NO ₃ -N	0.87	0.0001
8/19/93	Yld = 0.97 + 0.019 NO ₃ -N	0.79	0.0001
9/9/91	Yld = 1.16 + 0.033 NO ₃ -N	0.73	0.0001
9/23/91	Yld = 1.01 + 0.036 NO ₃ -N	0.73	0.0001
4/10/91	Yld = 0.96 + 0.030 NO ₃ -N	0.72	0.0001
9/29/92	Yld = 0.43 + 0.077 NO ₃ -N	0.70	0.001
1/11/94	Yld = -1.066 + 0.0097NH ₄ -N	0.58	0.0001
10/10/91	Yld = 1.17 + 0.064 NO ₃ -N	0.56	0.0001

@, *, ** - significant at the 0.10, 0.05 and 0.01 probability levels respectively.

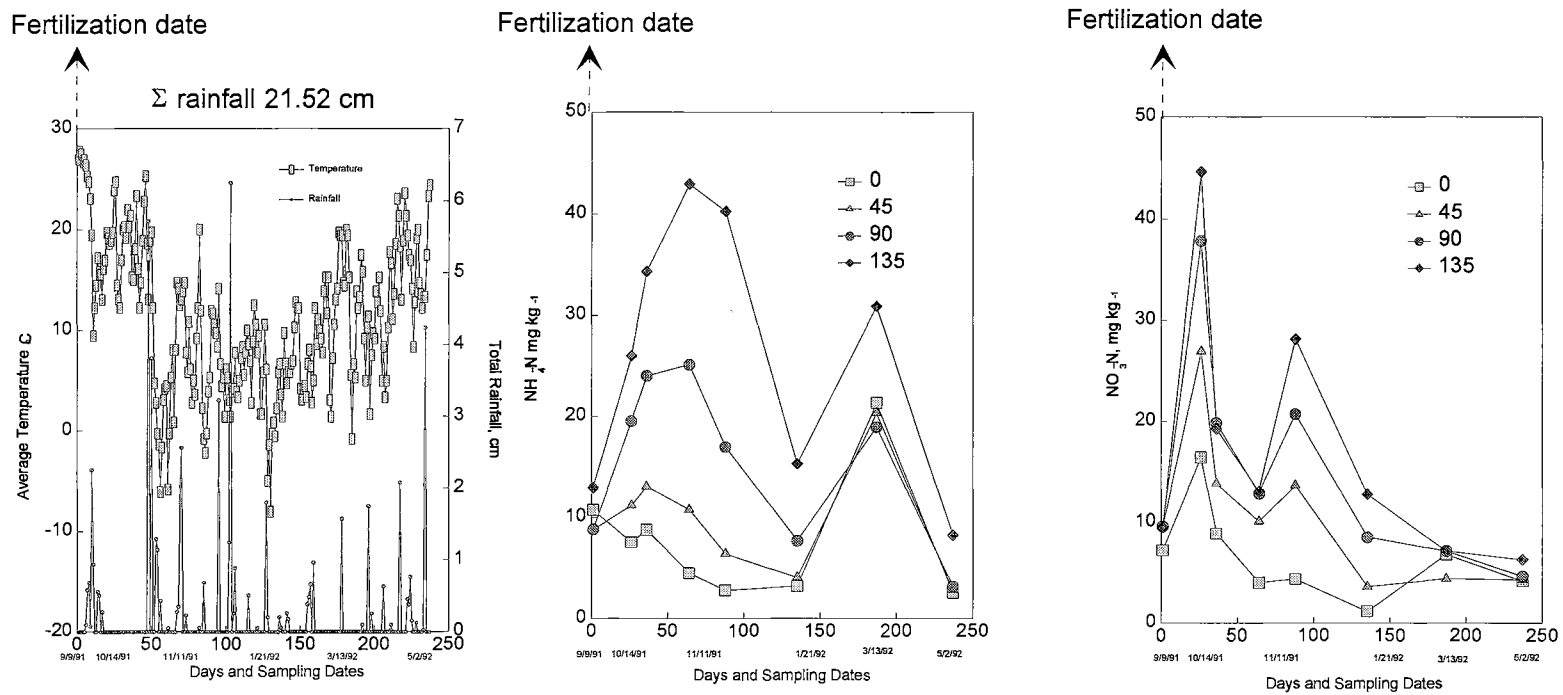


Figure 1. Daily average temperature and rainfall, changes in NH₄-N and NO₃-N, for the 1991-92 crop year, experiment 222 Stillwater, OK.

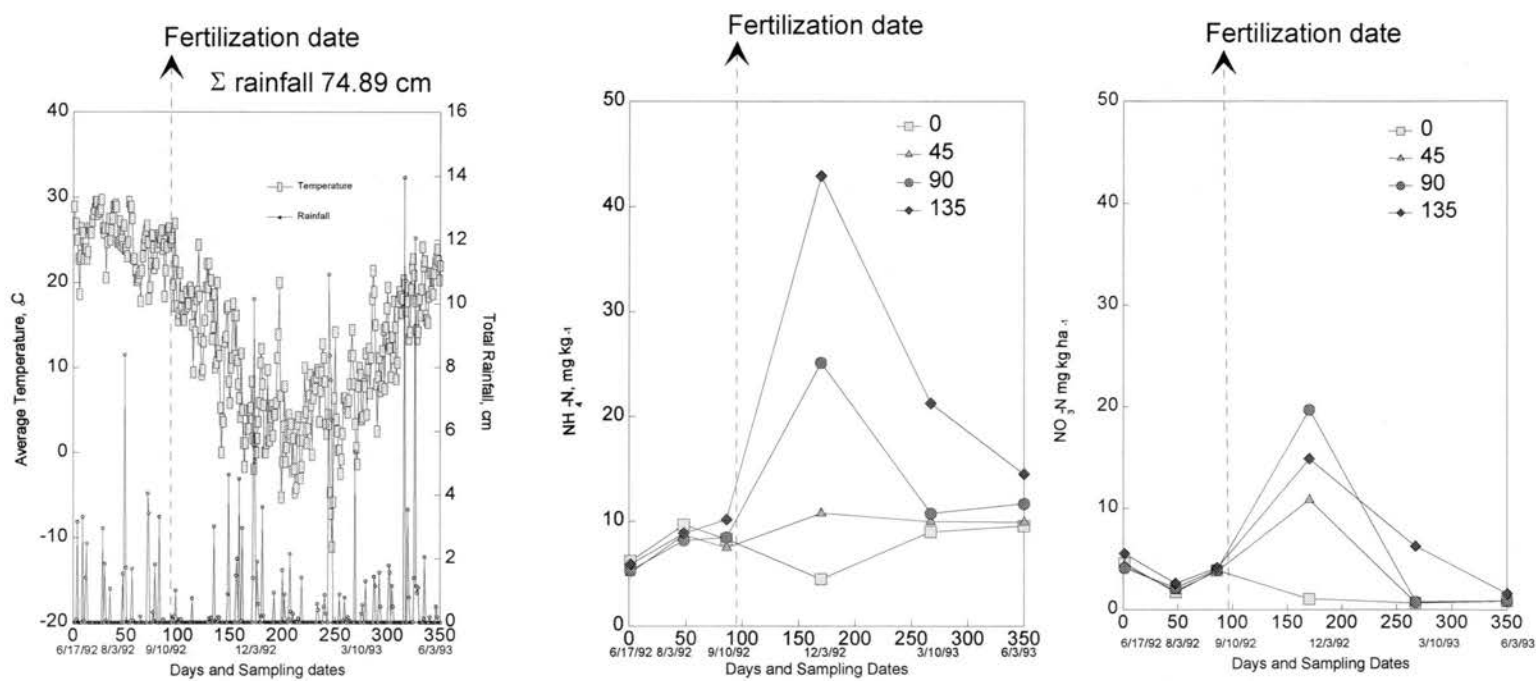


Figure 2. Daily average temperature and rainfall, changes in NH₄-N and NO₃-N, for the 1992-93 crop year, experiment 222 Stillwater, OK.

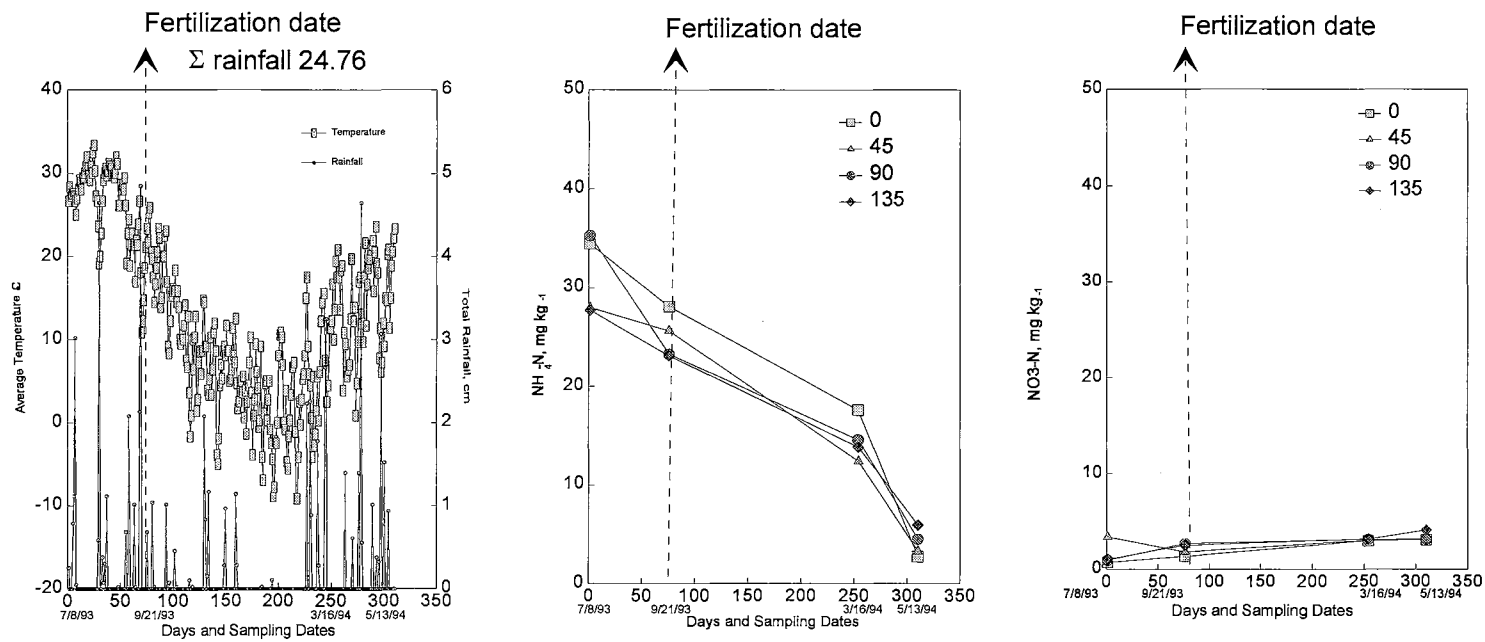


Figure 3. Daily average temperature and rainfall, changes in $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$, for the 1993-94 crop year, experiment, 222 Stillwater, OK.

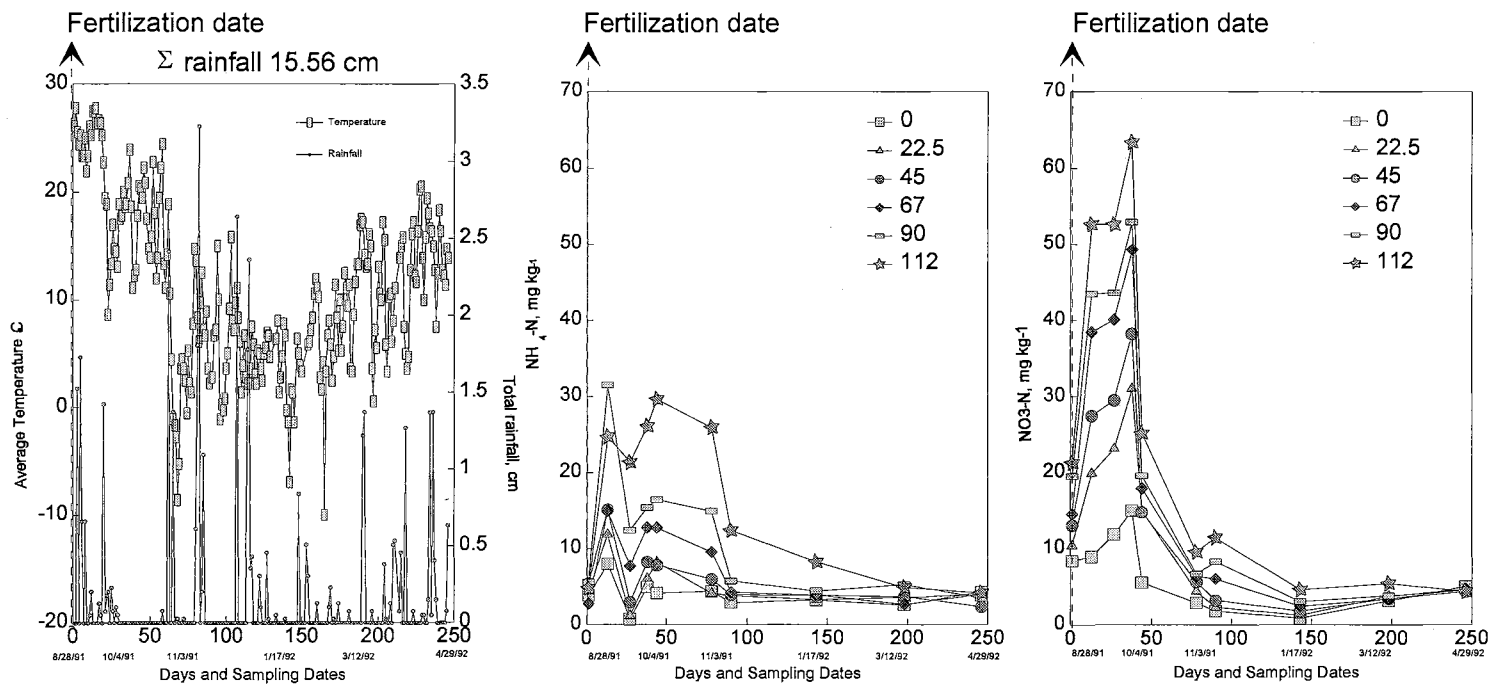


Figure 4. Daily average temperature and rainfall, changes in $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$, for the 1991-92 crop year, experiment 502 Lahoma, OK.

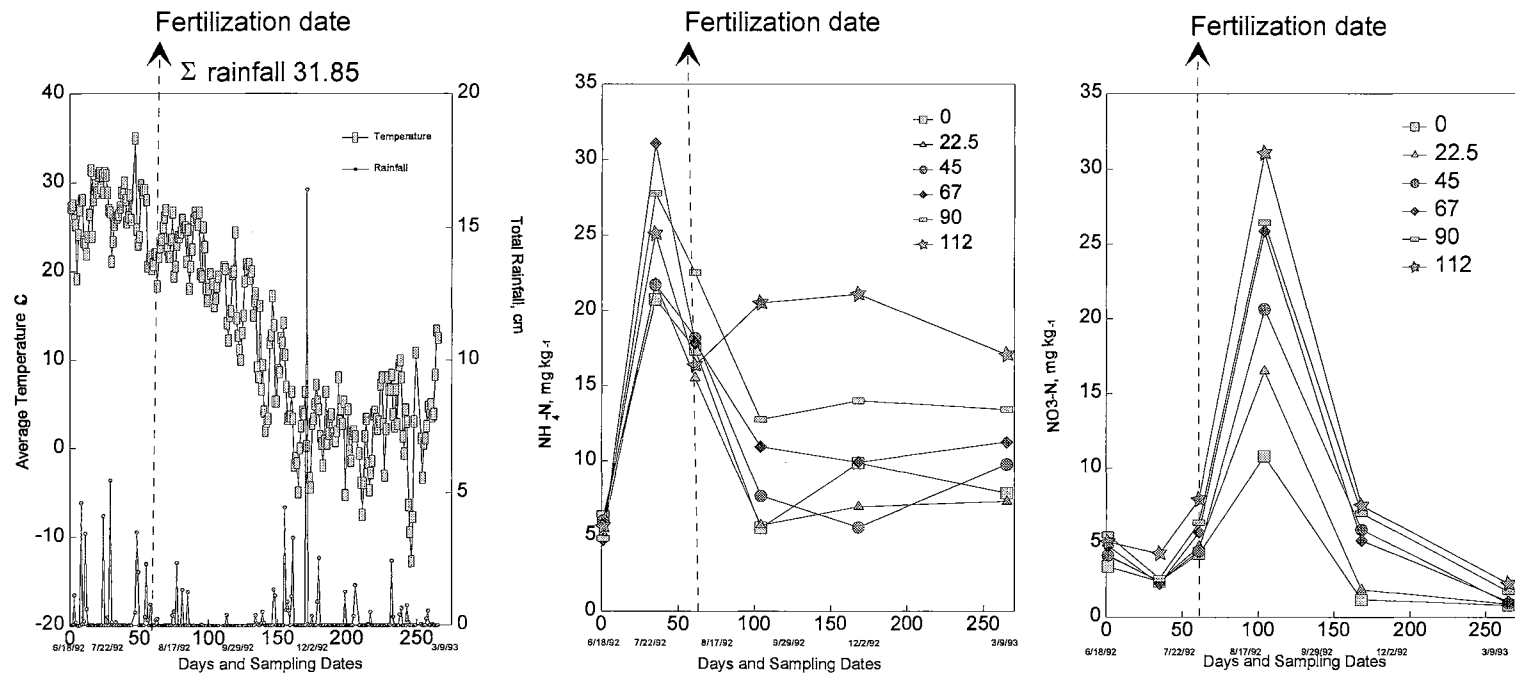


Figure 5. Daily average temperature and rainfall, changes in $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$, for the 1992-93 crop year, experiment 502 Lahoma, OK.

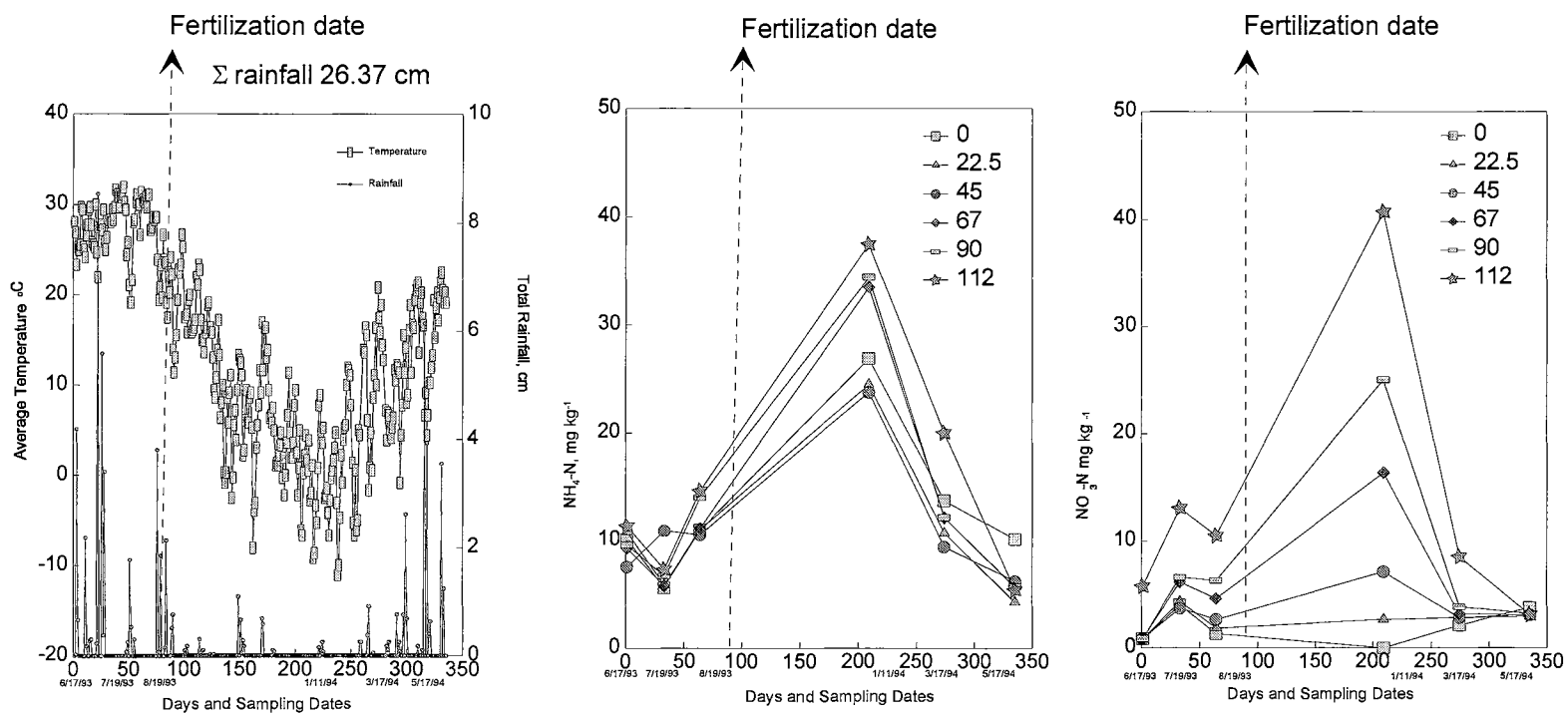


Figure 6. Daily average temperature and rainfall, changes in NH₄-N and NO₃-N, for the 1993-94 crop year, experiment 502, Lahoma, OK.

CHAPTER II

DISTRIBUTION OF SOIL PROFILE NO₃-N UNDER FLOODED CONDITIONS USING A BROMIDE TRACER

ABSTRACT

Nitrate-N in groundwater has been associated with the use of commercial fertilizers in continuous crop production systems. Risks associated with the use of commercial N fertilizers have not been established in terms of estimating movement with and without surface runoff. Two winter wheat field experiments were initiated to study nitrate and bromide movement in the soil profile as affected by water and N applied. Nitrogen and Br were applied at rates of 80 kg N and Br ha⁻¹ as KNO₃ and KBr, respectively. Metal frames 30 cm high by 1.5x1.5 m were buried 15 cm deep to prevent runoff. Paired treatments were used to evaluate the effects of applied water (7.6 cm/application) on three separate dates. Including natural precipitation, total water received in different treatments ranged from 11 to 52 and 11 to 118 cm at Lahoma and Perkins, respectively. Treatments were designed to accommodate destructive sampling for bulk density, nitrate and bromide analyses. Bromide recovery levels

decreased with time and water applied. Nitrate recovery levels were generally lower than bromide recovery levels which suggests potential denitrification losses under the near saturated conditions evaluated. On the final sampling date at Lahoma, N and Br recovery levels were > 58 % in plots having received 28 to 51 cm of total water (applied + precipitation). Plots receiving supplemental water were flooded for short periods of time, subsequently increasing the potential for denitrification losses. Because profile distribution patterns for NO₃-N were not altered based on only water applied, gaseous N losses must have taken place.

INTRODUCTION

The influence of soil type and climate on the movement of anions suggests the need for in-situ soil physical and chemical measurements and the use of local weather data when predicting their displacement. High yielding agriculture in modern times has been facilitated by new technologies including, the use of fertilizers which have greatly improved yields. In the United States the consumption of nitrogen fertilizer has grown from small amounts before 1945 to over 10⁷ Mg (as N) (Hallberg and Keeney, 1993). Increased concerns associated with NO₃-N pollution have paralleled the increased use of N fertilizers (Hallberg, 1987). As a result, substantial research has recently focused on the fate of N in soil-plant systems. An evaluation of four long-term experiments under continuous winter wheat showed that whenever N is applied at the

recommended rates $\text{NO}_3\text{-N}$ accumulation in sub-surface soil profiles was not different from that found where no N was applied (Westerman et al., 1994). Chaney (1990) studied several N fertilizer rate experiments in winter wheat and concluded, based on the nitrogen remaining in the soil after harvest, that $\text{NO}_3\text{-N}$ increased only when fertilization rates exceeded the economic optimum.

The term spatial variability is defined by the Soil Science Society of America (1987) as the variation in soil properties in a lateral sense across the landscape at a given depth or with a given horizon or in a vertical sense downward through the soil. Several studies have shown that the movement of anions in soils is influenced by several factors including soil structure, texture, water infiltration, plant roots etc. (Chan and Mead, 1989, Andreini and Steenhuis, 1990). Starr and Glofelty (1990) indicated that the downward displacement of agrochemicals in the soil to groundwater is influenced by soil properties, soil management, timing of leaching events and the dynamics of the transformation processes. Miller and Gardner (1962) studied the effects of textural and structural stratification of a soil profile on downward water movement and found that the rate of infiltration of a wetting front is affected by the size of the soil pores encountered. Silvertooth et al. (1992) indicated that site specific spatial variability would have to be considered for any regulatory program that evaluates $\text{NO}_3\text{-N}$ at a specific point in the soil profile.

Bromide is one of the most widely used tracers in hydrology research and in the study of movement of agrochemicals through the soil. In hydrology, a

tracer can be matter or energy carried by water which will provide information concerning the direction and/or velocity of the water as well as potential contaminants which could be transported by water (Davis et al. 1980). Movement of bromide in soils has been compared to movement of $\text{NO}_3\text{-N}$ in different studies. Bromide can act as tracer for $\text{NO}_3\text{-N}$ because of its similar movement as compared to $\text{NO}_3\text{-N}$, it is also found in low concentration in soils and irrigation water, is highly soluble, is not toxic to plants at low concentrations and is inexpensive (Onken et al, 1975). Adriano and Doner (1982) indicated that the content of bromide in mineral soils average about $6 \mu\text{g g}^{-1}$ (range from 0.3 to $40 \mu\text{g g}^{-1}$ of Br^-) and in peats approximately 30 ppm (range from 12 to 70 ppm of Br^-).

Movement of chemicals in the soil has been studied for many years. This research forms the basis for technology that is presently available to predict the movement and degradation of chemicals in soils (Nofziger, 1989). The ability of some models to predict chemical movement has been tested separately and collectively (Pennell et al., 1990). This same author indicated, that although considerable effort has been expended to develop pesticide simulation models, comparatively little work has been done to validate these models using independent data sets. Hornsby and Rao (1990) also mentioned that lack of appropriate field data sets and companion laboratory data continues to be a major limitation to development, validation and use of simulation models. When predicting chemical movement, several principles have to be kept in mind.

Chemicals tend to move with the soil water, therefore quantification of water movement in soils is essential for predicting chemical movement and chemicals tend to be adsorbed physically or chemically to solid soil surfaces. This retention process tends to increase the residence time of the chemical in the soil and slows down its movement. Nofziger (1989) noted that chemicals tend to undergo biological and chemical transformations in the soil. Work by Addiscott (1991), found that leaching of nitrate is governed by three main processes: 1) water flowing through the soil, which tends to wash the nitrate out, and 2) the microbial activity in the soil, which produce nitrate as they break down nitrogen-containing organic material in the soil, and that can remove nitrate from the system by locking it up in soil organic material or by converting it to gaseous nitrogen or nitrous oxide, and 3) crops growing on the soil, which can assimilate nitrate and remove it, thus reducing the risk of leaching.

Nitrate-nitrogen in the soil is produced during the process of nitrification. This process is carried out mainly by two groups of bacteria. The first group of bacteria known as Nitrosomonas, convert NH_4^+ to NO_2^- . The next step is brought about mainly by Nitrobacter, which oxidizes NO_2^- to NO_3^- (Tisdale et al, 1985). Studies have shown that populations of nitrosomonas may increase from one hundred to several hundred million per gram of soil upon the addition of ammonium fertilizer. Similar results can be shown in the growth of nitrobacter upon the addition of nitrite to soil (Focht and Verstraete,1977). However, nitrification is not the only process contributing NO_3^- to the soil. A less

significant contribution, nitric oxide is produced in the atmosphere surrounding lightning discharges, which is ultimately transformed to NO_3^- by photochemical oxidation and deposited in rainfall (Schmidt, 1982). Even though nitrification has been adequately predicted by using kinetic approaches, its applications are scarce when considering that rate constants must often be modified by such factors as soil temperature, soil moisture, soil pH, and substrate loading rates (Honeycutt, et al.1991). When $\text{NO}_3\text{-N}$ is produced at the end of the mineralization process, it can be taken up by the plant, immobilized in organic fractions, denitrified and leached.

It is considered that plant uptake of N fertilizer is low, being approximately 50% but can range from 20-80% (Viets, 1977). Tisdale et al. (1985) consider the immobilization of nitrogen as the reverse of the mineralization process, and it occurs when considerable quantities of low-nitrogen crop residues begin decomposing in the soil. Nitrate-nitrogen is used in this case to build up cells in the increasing population of microflora. Hallberg and Keeney (1993) said that even though nitrates are involved in the immobilization phase of the nitrogen cycle, heterotrophs strongly prefer ammonium if available.

Losses of nitrogen from the soil in the form of gas occur mainly as nitrous oxide (N_2O) and dinitrogen (N_2), whenever reductive (denitrification) and oxidative (nitrification) processes occur (Tisdale et al, 1985). Gaseous N loss can also take place via decomposition of nitrite under aerobic conditions which produces N_2 , NO plus NO_2 , and small quantities of N_2O .

Tisdale et al (1985), describe denitrification as a process performed by some anaerobic organisms that obtain their oxygen from nitrates and nitrites, releasing nitrogen and nitrous oxides in the process. Most of the denitrification process is not clearly known at present, consequently denitrification losses of N have not been accurately determined. However, according to Addiscott (1991), denitrification becomes important when considering NO_3^- pollution problems because NO_3^- subject to denitrification is not going to leach. Anaerobic conditions that lead to denitrification are produced by the displacement of air for water in the soil and under well aerated conditions oxygen must move freely into it and carbon dioxide out (Currie, 1961). Organic carbon in the soil is also associated with denitrification as “hot spots”, and high specific denitrification activity has been associated with particulate organic material (Parkin, 1987). Korom (1991), stated that during heterotrophic denitrification in a saturated zone, organic matter is the most common electron donor, and thermodynamically in the chain NO_3^- is the next preferred whenever dissolved oxygen is removed. Autotrophic denitrification takes place whenever NO_3^- is introduced into a manganese/iron or sulfate reducing zone (Korom, 1992).

As per the work of Keeney, (1982), optimum N fertilization rates are influenced by several site-specific conditions and by climate. Therefore, the objective of this study was to determine the potential movement of nitrate using a bromide tracer as a function of water applied and time at two sites representative of winter wheat production of Oklahoma.

MATERIALS AND METHODS

Two locations were selected to evaluate $\text{NO}_3\text{-N}$ accumulation in soil profiles as affected by amount of water applied and frequency of application. The experimental sites were at Perkins, OK (Teller sandy loam, fine-loamy, mixed, thermic Udic Argiustoll) and Lahoma, OK (Grant silt loam fine, mixed, thermic, Udic Argiustoll). The experiment at Perkins was initiated on November 18, 1992 and on May 10, 1994 at Lahoma. Initial surface soil test analysis at each location is reported in Table 1. At both locations, soil $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ were determined using an automated flow injection analysis system, following extraction with 2 M KCl (2 g samples). Bromide analysis was determined using ion chromatography (method 300.0, U.S. EPA, 1993).

Perkins

The experimental site consisted of 81 m² and was located in the middle of a large wheat field with a slope of 1.5 %. This experimental area had been grown to continuous winter wheat for the past 15 years without N fertilization. The depth to water table in the closest well was measured at 3.25 m. A randomized complete block experimental design was employed, whereby specific plots containing groups of treatments were sampled on the same dates, but which received different amounts of applied water. Winter wheat (Triticum

aestivum.) 'Karl' was planted on October 9 at a rate of 67.2 kg ha^{-1} . Visual N deficiencies were notable at this site in previous years. Metal frames $1.5 \times 1.5 \text{ m}$ and 0.254 m high were constructed by using 3 mm thick steel. The frames represented individual plot sizes whereby each one was buried approximately 15 cm . (10.4 cm above ground) to prevent any surface runoff and/or any outside contamination. All experimental plot frames were put in place once an established wheat stand was present. Treatments consisted of two levels of bromide (80 and $200 \text{ kg Br ha}^{-1}$), two levels of nitrogen (80 and 200 kg N ha^{-1}) and 7.6 cm of water applied at different dates, 0 , 15 and 70 days after treatments were applied respectively. The sources of NO_3^- and Br^- were KNO_3 and KBr respectively. Treatment structure, water application and sampling dates are listed accordingly in Table 2. Soil samples were taken from a check plot to determine background levels of Br^- and NO_3^- prior to treatment application. Samples for bulk density were also obtained in each experimental unit. Treatments 1-2, 3-4, 5-6, 7-8 and 9-10 were sampled on the same date but the latter treatment in each group received water only as natural precipitation. Soil core sampling dates for each treatment are reported in Table 2. On each sampling date, four cores were taken per plot for bulk density and particle size analysis (split in increments of $0\text{-}15$, $15\text{-}30$, $30\text{-}45$, $45\text{-}60$, $60\text{-}90$, $90\text{-}120$, $120\text{-}150$, $150\text{-}180 \text{ cm}$) whereby each increment from each core was analyzed and recorded separately. Two additional cores were taken for chemical analysis in each plot at each sampling date to a depth of 180 cm , and split in increments of

0-15, 15-30, 30-45, 45-60, 60-90, 90-120, 120-150, and 150-180, cm for Br⁻¹, NO₃-N, NH₄-N, total N and organic carbon analysis. Wheat growing inside plots containing treatments were harvested for grain and straw yield to determine N accumulation.

Lahoma

The second experiment was initiated on April 14, 1994 at the North Central Research Station near Lahoma, OK. Treatment levels of nitrogen and bromide included two levels of bromide (0 and 80 kg Br ha⁻¹), two levels of nitrogen (0 and 80 kg N ha⁻¹) and 7.6 cm. of water applied at different dates after treatments were applied (Table 3). The experimental area was approximately 160 m² and this area had been cropped to winter wheat without fertilization for the past 10 years. The same metal frames used at Perkins (1.5 x 1.5 m and 0.254 m high) were used at Lahoma. Treatment structure was altered such that instead of having one check plot for all treatments, independent by-date check plots were included where no KBr or KNO₃ were applied. The reason for this was due to the large difference in NO₃-N concentration found in the soil of the check plots at Perkins at the beginning and at the end of the experiment. This finding suggested that the N mineralization process had to be considered when sampling at different dates. Therefore, when plots containing a set of treatments was sampled on a certain date, a check plot was also sampled. One

additional treatment was also added as a bromide check. For this treatment, plots were covered immediately after the application of N ($80 \text{ kg NO}_3\text{-N ha}^{-1}$), Br (80 kg Br ha^{-1}) and 25 mm of water. These plots served to identify any bias that may have been present from chemical and physical (bulk density) analyses conducted at the end of the experiment since these would have a theoretical recovery level of 100%. Another new modification at the Lahoma site was the inclusion of plots 3x5 randomly located in the experiment. These treatments consisted of a check plot (0N and 0 Br) and a paired plot receiving 80 kg N ha^{-1} and 80 kg Br ha^{-1} . These treatments were used to observe displacement of NO_3^- and Br^- under natural conditions without artificial water application and where water received was not artificially retained at the surface by a metal frame around the plot. Every treatment group (1-3, 4-6, 7-9 and 10-12) had a respective check plot (3, 6, 9 and 12, respectively) that was sampled the same day. Bulk density and particle size analysis samples were taken in the same way as at Perkins (4 cores per plot to a depth of 180 cm). Two cores were also taken for chemical analysis to a depth of 180 cm, sectioned, recorded and analyzed as described above for the first experiment. Bromide and N recovery were determined by first calculating soil profile accumulation (Br and NO_3^- concentration converted to kg ha^{-1} using measured bulk density to a depth of 180 cm), and then subtracting accumulation amounts in the check and dividing by the rate applied.

RESULTS AND DISCUSSION

Perkins

Significant differences between treatments were found for soil accumulation of $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and Br^{-1} (Table 4). Similar results were also noted for the sum of $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and Br in the entire profile (Table 5). The treatment by depth interaction was also significant for soil Br but not for $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$. Because sampling encompassed different dates, timing of movement of solutes in the soil and dynamics of transformation processes were expected to affect the treatment by depth interactions of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$, especially when compared to check plots. The day the experiment was initiated (11/18/94) treatment 11 (N0B0, check plot) was sampled in order to determine background levels of $\text{NO}_3\text{-N}$ and Br. Treatment 12 (N0B0) was an identical check plot, but plots containing it were sampled at the end of the experiment. Although no Br was detected at any depth either at the beginning or end of the experiment, surface $\text{NO}_3\text{-N}$ levels were significantly different (Figure 1). Considering that no fertilizer has been applied at this site for over 15 years, it was interesting to find such large fluctuations in surface $\text{NO}_3\text{-N}$ over this 262 day period.

Plots that have received treatments 1 (N1B1 + 18.7 cm of water) and 2 (N1B1 + 11.1 cm water) were sampled on December 3, 1992, fifteen days after

the KNO_3 and KBr were applied. Both treatments consisted of applying 80 kg of Br and N ha^{-1} . In addition to the 7.6 cm of water applied to plots selected for treatment 1 on November 18, 1992, an additional 11.09 cm of natural precipitation was received. A significant increase in subsurface $\text{NO}_3\text{-N}$ and Br was found in the profile of plots embodying treatment 1 which received an additional 7.6 cm of water (Figure 2). Movement of Br to the 120 cm depth fifteen days following treatment application with 18.7 cm of total precipitation clearly shows the potential for leaching in this soil. This is especially true when compared to plots receiving treatment 2, where Br could not be detected at depths greater than 90 cm. However, $\text{NO}_3\text{-N}$ accumulation patterns in plots holding treatments 1 and 2 were virtually identical as were estimates of total N accumulated in the 0-180 cm profile (Figure 2 and Table 6). This suggests that Br provided a poor example of what would likely happen to $\text{NO}_3\text{-N}$ in the profile since the effect of water applied was markedly different in both. This is also supported by the high background levels of $\text{NO}_3\text{-N}$ found in these profiles at the start of the experiment (Figure 1). Estimates of N and Br recovery exceeded 76% for both treatments and differences between treatments 1 and 2 were small (<6%, Table 6). Assuming that increased water applied should displace or leach greater quantities of Br, it should be noted that even though recoveries were less than 100%, total accumulation amounts were not different between treatments 1 and 2, suggesting that no Br at this point had been leached through the profile.

Recoveries being less than 100 % at this point were likely a cause of bias in both bulk density and concentration estimates.

Plots accommodating treatments 3 (N1B1 + 56.1 cm of water) and 4 (N1B1 + 40.9 cm water) were sampled on January 28, 1993, 70 days after KNO_3 and KBr application. Treatments 3 and 4 differed in total water received by 15.2 cm over this 70 day period when the plots were sampled. It was interesting to note a significant difference in $\text{NH}_4\text{-N}$ accumulation at the 90 cm depth where less water was applied (treatment 4, Figure 3). In a study of semiarid soils, Bower (1950) found that 14 of 21 samples fixed appreciable quantities of ammonium under moist conditions, and that fixation was higher at depths of 2 to 5 feet than in the surface. More recently, Baethgen and Allen, (1986) while studying Virginia soils also suggested that ammonium fixation by clay minerals was larger in the subsoil because of the higher clay content. It is also known that soils rich in 2:1 clay minerals such as vermiculite, illite and in some cases montmorillonite, may contain large amounts of non-exchangeable $\text{NH}_4\text{-N}$ as NH_4^+ ions trapped in the interlayer spaces of these clay minerals (Baethgen and Allen, 1986). Unlike results obtained 15 days following treatment applications, by 70 days, increased water applied resulted in higher subsoil accumulation of both Br and $\text{NO}_3\text{-N}$, especially at depths > 90 cm (Figure 3). Given the controls used in the experiment, this showed the direct impact of excess water where no runoff was encountered, and when water is applied in winter months when surface evapotranspiration is limited. Problems associated with estimated

recovery are evident in Table 6 since values exceeded 100% for N (both treatments) while being less than 63% for Br 70 days after fertilizers were applied (treatments 3 and 4). Onken et al. (1977), while studying the relative movement of bromide and nitrate in soils under three irrigation systems concluded that nitrate and bromide had moved together in the soil profile, but the concentrations of $\text{NO}_3\text{-N}$ and Br were quantitatively unrelated. They pointed out some reasons for this incongruent relationship (i) $\text{NO}_3\text{-N}$ was the sum of that already present, that from mineralization of organic matter, plus that applied while bromide came only from that applied, and (ii) $\text{NO}_3\text{-N}$ from all three of these sources and Br^{-1} , were removed from the soil at different rates by the growing crop.

The continued movement of Br was observed when comparing results from Figure 3 to that of Figure 4. From Jan 28 to March 3, 54.9 cm of natural precipitation was received. At seventy days following the application of Br, only limited amounts could be detected at the 150 cm depth. However, by 105 days, Br was detected at the 180 cm depth (Figure 4). Because no background Br levels were detected in either check plot (Figure 1 and Table 6), movement per unit water applied could be assessed. It is interesting to note, however, that even though significant quantities of Br were found at the 180 cm depth in plots receiving treatment 5, the total profile accumulation amounts were not different when compared to treatment 6 (Table 6). This is important as it suggests that following 105 days with > 63.7 cm of rainfall, no Br had actually been removed

from the profile (0-180 cm). Similar to Br, total $\text{NO}_3\text{-N}$ profile accumulation did not differ between treatments 5 and 6 (Table 6) and accumulation patterns were similar even though the total water applied differed by more than 50% (Figure 4). Although Br recovery levels remained low, they were not significantly different between treatments. Again, this suggests that recovery estimates were biased (should have been 100%) since the increased water applied should have reduced recovery in treatment 5. Because there were no differences, increased leaching/loss in one or the other could not be inferred.

Plots accommodating treatment 7 (N2B2 + 118.3 cm of water), treatment 8 (N2B2 + 95.5 cm water), treatment 9 (N1B1 + 118.3 cm of water) and treatment 10 (N1B1 + 95.5 cm water) were sampled on July 5, 1993. Plots including treatments 7 and 8 received a high rate of nitrogen and bromide (200 kg ha^{-1}), while plots receiving treatments 9 and 10 received the low rate (80 kg ha^{-1}) identical for treatments 1-6. The existence of a clay layer where increased ammonium fixation was taking place continued to be evident at this site for treatment 7 (Figure 5). However, this increased $\text{NH}_4\text{-N}$ was not observed for all treatments.

Nitrate-N in the soil profile tended to be higher in plots with treatments 8 and 10 where no water was applied, when compared to plots that had received the same respective treatments but had received added water (treatments 7 and 9, Figure 5). A similar trend was noted for Br applied at the high rate (treatment 7 versus 8), but the same was not observed at the lower Br rate at the end of the

experiment (Table 6 and Figure 5). According to Nofziger, 1989, chemicals tend to move with the soil water. Both $\text{NO}_3\text{-N}$ and Br recovery levels were small for treatments 7, 9 and 10 (Table 6). However, recovery levels were much greater in plots having treatment 8 than those plots containing treatment 7 which received 22.8 cm less water (95.5 versus 118.3 cm) over this 262 day period. It is not understood how 20 % less water applied (95.5/118.3) could result in 2x recovery level differences (Table 6). Because the supplemental water was all applied at one time, there were significant time periods when treatments receiving the added water were flooded and essentially under water (up to 3 days). Paired plots not receiving supplemental water, but which received natural precipitation, were never flooded as rainfall amounts did not lead to conditions where water was left standing on the surface. Because of this, extended periods which led to the reduced conditions in the plots receiving supplemental water may have increased both N (denitrification) and Br loss.

Lahoma

Differences between treatments were found for soil accumulation of $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and Br (Table 4). Similar results were also noted for the sum of $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and Br in the entire profile (Table 5). The treatment by depth interaction was significant for $\text{NH}_4\text{-N}$, thus simplifying the main effect interpretation of treatment for this variable.

Unlike Perkins, by-date treatments were included in an attempt to improve the accuracy of accumulation and percent recovery estimates. This was largely because of the differences noted in profile $\text{NO}_3\text{-N}$ accumulation with no fertilization over a 262 day period at Perkins. Similar to Perkins, continuous winter wheat was produced at this site for more than 25 years without fertilization. Because of this, background levels of $\text{NO}_3\text{-N}$ in the May 10 check plots (treatment 3) were much smaller than that observed at Perkins. Plots containing treatments 1 (N1B1 + 18.9 cm of water), 2 (N1B1 + 11.3 cm water) and 3 (N0B0 + 11.3 cm water) were sampled on May 10, 1994, 26 days after the KNO_3 and KBr were applied. Plots embodying Treatments 1 and 2 received 80 kg of Br and N ha^{-1} while treatment 3 was applied to plots that served as the by-date check with no Br or N. In addition to the 7.6 cm of water included as a part of treatment and applied on April 14, 1994, an additional 11.3 cm of natural precipitation was received by the first sampling on May 10. Surface $\text{NO}_3\text{-N}$ and Br levels both increased in proportional amounts when observing all profiles 0-60 cm that received either N or Br. An accumulation bulge was found at the 30 cm depth whether or not additional water was applied. It was interesting to find decreased total $\text{NO}_3\text{-N}$ profile accumulation when additional water was applied (treatment 1) compared to plots containing treatment 2 which only received natural precipitation. Because plots receiving additional water were flooded for at least 2 to 3 days, denitrification losses would help explain the differences observed in Figure 7. However, the predominance of soil temperatures between

15 and 25 °C during this time period may have enhanced anaerobic microbial activity and led to significant amounts of immobilized fertilizer N. These results are somewhat alarming since estimated N recovery where added water was applied was 18%, compared to 86% where no water was applied 26 days after the KNO₃ was applied (Table 7). Of equal importance was the 50% recovery for Br noted at the same time.

Only twenty days after the first sampling reported in Figure 7, estimated N recovery dropped to 6% while Br recovery increased to 77% in plots that had received both additional precipitation (14.32 cm) and an intentional irrigation (7.62 cm, Figure 8 and Table 7). By the June 1 sampling date (46 days after treatment application), estimates of Br recovery were lower in plots of treatment 4 where more water was applied compared to plots of treatment 5 which received only natural precipitation. As would be expected, the accumulation bulge for Br was now found at 60 cm in treatment 4, but which was previously at 30 cm for treatment 1, 20 days earlier (Figures 7 and 8). Where a total of 40.8 cm of water was received (precipitation + applied), increased NO₃-N could no longer be detected in the soil profile when compared to the by-date check (Figure 8). Differences in NH₄-N were generally found to be small.

Sixty one days after treatment application, differences in soil profile NH₄-N remained small (Figure 9). Because only limited precipitation was received from June 1 to June 15, soil profile NO₃-N and Br were much the same when comparing Figures 8 and 9. By 74 days, treatment 10 resulted in an estimated N

recovery of 223% (Table 7, and Figure 10). This experimental site was located in between two long-term fertilizer experiments which were initiated in 1971. It is possible that an accidental fertilizer spill took place in this area, which caused the elevated recovery. Bromide recoveries were realistic, with levels being much lower where added water was applied versus natural precipitation. Treatment 13 provided an important comparison, since N and Br were applied at the same rates as treatments 1,2,4,5,7,8,10 and 11, but that received no added water (other than 2.5 cm to mix the N and Br into the surface of the soil). In addition, all three plots comprising treatment 13 were immediately covered whereby no precipitation was received from April 14 to June 29 when the experiment was completed. Following this 74 day period, estimated Br recovery was 14% which suggests that biological immobilization or some other transformation took place within the soil. Because plants also did not grow during this time, and because leaching would have been impossible, the formation of organic Br forms must have taken place which would not have been detected in the extract.

CONCLUSIONS

Results from this work conducted at two different locations and under substantially different environmental conditions suggest that Br movement does not properly characterize what takes place when $\text{NO}_3\text{-N}$ fertilizers are applied. This is especially true when reduced conditions are present for short periods of

time. This work suggests that denitrification losses were highly significant when the metal frame experimental units were flooded. Significant bias error was encountered when estimating Br recovery, further suggesting the need for alternative tracer methods. The use of stable ^{15}N isotopes would probably be ideal, however, this technology is extremely expensive.

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Table 1. Initial soil test levels, Perkins and Lahoma, OK.

Location	pH	P mg kg ⁻¹	K mg kg ⁻¹	Organic C g kg ⁻¹	Total N g kg ⁻¹
Perkins	6.1	11	148	6.8	0.52
Lahoma	5.0	45	320	7.1	0.62

Table 2. Treatment structure, water application and sampling dates, Perkins, OK, 1992-1993.

Treatment	N rate kg ha ⁻¹ as KNO ₃	Br rate kg ha ⁻¹ as KBr	--- Water applied cm -----			Soil core sampling date
			11/18/92	12/3/92	1/28/93	
1	80	80	7.6			Dec./3/92
2	80	80				Dec./3/92
3	80	80	7.6	7.6		Jan./28/93
4	80	80				Jan./28/93
5	80	80	7.6	7.6	7.6	Mar./3/93
6	80	80				Mar./3/93
7	200	200	7.6	7.6	7.6	July/5/93
8	200	200				July/5/93
9	80	80	7.6	7.6	7.6	July/5/93
10	80	80				July/5/93
11	0	0				Nov./18/92
12	0	0				July/5/93

Table 3. Treatment structure, water application and sampling dates, Lahoma, OK, 1994.

Treatment	N rate kg ha ⁻¹ as KNO ₃	Br rate kg ha ⁻¹ as KBr	---Water applied cm -----			Soil core sampling date
			4/14/94	5/10/94	6/1/94	
1	80	80	7.6			May/10/94
2	80	80				May/10/94
3	0	0				May/10/94
4	80	80	7.6	7.6		June/1/94
5	80	80				June/1/94
6	0	0				June/1/94
7	80	80	7.6	7.6	7.6	June/15/94
8	80	80				June/15/94
9	0	0				June/15/94
10	80	80	7.6	7.6	7.6	June/29/94
11	80	80				June/29/94
12	0	0				June/29/94
13	80	80	2.53©			June/29/94
14	80	80	♣			June/29/94
15	0	0	♣			June/29/94

© Plot covered

♣ Field conditions, no metal frame

Table 4. Analysis of variance for soil profile NH₄-N, NO₃-N and Br in kg ha⁻¹, Perkins and Lahoma, OK

Source of variation	df	Mean NH ₄ -N	Squares NO ₃ -N	Br
Perkins				
Replication	2	567.07	450.29	1.16
Treatments	11	1206.05**	873.50**	418.45**
Replication*Treatment (a)	22	662.63	629.88	65.44
Depth	7	4842.08**	9422.30**	647.86**
Treatment*Depth	77	215.87	407.22	127.37**
Residual error	168	252.70	318.71	33.26
CV, %		49	56	110
Lahoma				
Replication	2	855.70**	487.75**	115.35
Treatments	14	1303.32**	733.51**	369.50**
Replication*Treatment (a)	28	391.22	367.91	85.93**
Depth	7	251.16**	212.89**	1216.70**
Treatment*Depth	98	54.44	165.73**	138.55**
Residual error	174	44.07	69.67	48.33
CV, %		40	95	157

** , * - significant at the 0.01 and 0.05 probability levels, respectively, CV - Coefficient of variation, df - degrees of freedom

Table 5. Analysis of variance for the sum of NH₄-N, and NO₃-N and Br in soil profiles, Perkins and Lahoma, OK

Sources of variation	df	Mean squares		
		NH ₄ -N	NO ₃ -N	Br
Perkins				
Replication	2	4336	3602	9
Treatments	11	9648	6988*	3347*
Residual error	22	5301	5039	523
SED		59	58	19
Lahoma				
Replication	2	4696	4788	1299
Treatments	14	9405	5980*	2991*
Residual error	28	3360	2991	613
SED		47	45	20

**, * - significant at the 0.01 and 0.05 probability levels, respectively, CV - Coefficient of variation, df - degrees of freedom, SED - Standard error of the difference between two equally replicated means

Table 6. Total water applied, rainfall, soil profile NO₃-N and Br and percent, recovery, Perkins, OK, 1992-93

Treatment	Interval days δ	Rainfall cm \uparrow	Total water cm \uparrow	Profile NO-N kg ha ⁻¹	Profile Br kg ha ⁻¹	N recovery %	Br recovery %
1	15	11.1	18.7	191	64	83	80
2	15	11.1	11.1	185	62	76	77
3	70	40.9	56.1	212	38	110	47
4	70	40.9	40.9	213	51	111	63
5	105	40.9	63.7	160	41	45	51
6	105	40.9	40.9	145	38	26	47
7	262	95.5	118.3	162	55	19	27
8	262	95.5	95.5	243	121	59	60
9	262	95.5	118.3	108	16	-20	20
10	262	95.5	95.5	114	19	-13	23
11✓	0	-	I	-	0	-	0
12✓	262	95.5	95.5	124	0	-	0

δ -days after KNO₃ and KBr were applied

I-initiation of experiment

Table 7. Total water applied, rainfall, profile NO₃-N and Br and percent recovery, Lahoma, OK, 1994.

Treatment	Interval days δ	Rainfall cm \dagger	Total water cm \dagger	Profile NO ₃ -N kg ha ⁻¹	Profile Br kg ha ⁻¹	N recovery %	Br recovery %
1	26	11.32	18.94	43.12	40.04	18	50
2	26	11.32	11.32	97.2	88.77	86	111
3 ✓	26	11.32	11.32	28.61	0	-	-
4	46	25.64	40.88	39.12	61.54	6	77
5	46	25.64	25.64	104.99	81.98	88	102
6 ✓	46	25.64	25.64	34.15	0	-	-
7	61	28.32	51.18	56.74	61.76	26	77
8	61	28.32	28.32	64.54	62.76	35	78
9 ✓	61	28.32	28.32	36.23	0	-	-
10	74	28.32	51.18	228.69	34.64	223	43
11	74	28.32	28.32	96.35	52.38	58	65
12 ✓	74	28.32	28.32	49.53	0	-	-
13 ©	74	0	0	123.87	11.13	87	14
14 ♣	74	28.32	28.32	57.87	11.68	5	15
15 ♣	74	28.32	28.32	53.73	0	-	-

✓ check plots

δ days after K and Br were applied

© plot covered

♣ field conditions, no metal frame

† cumulative

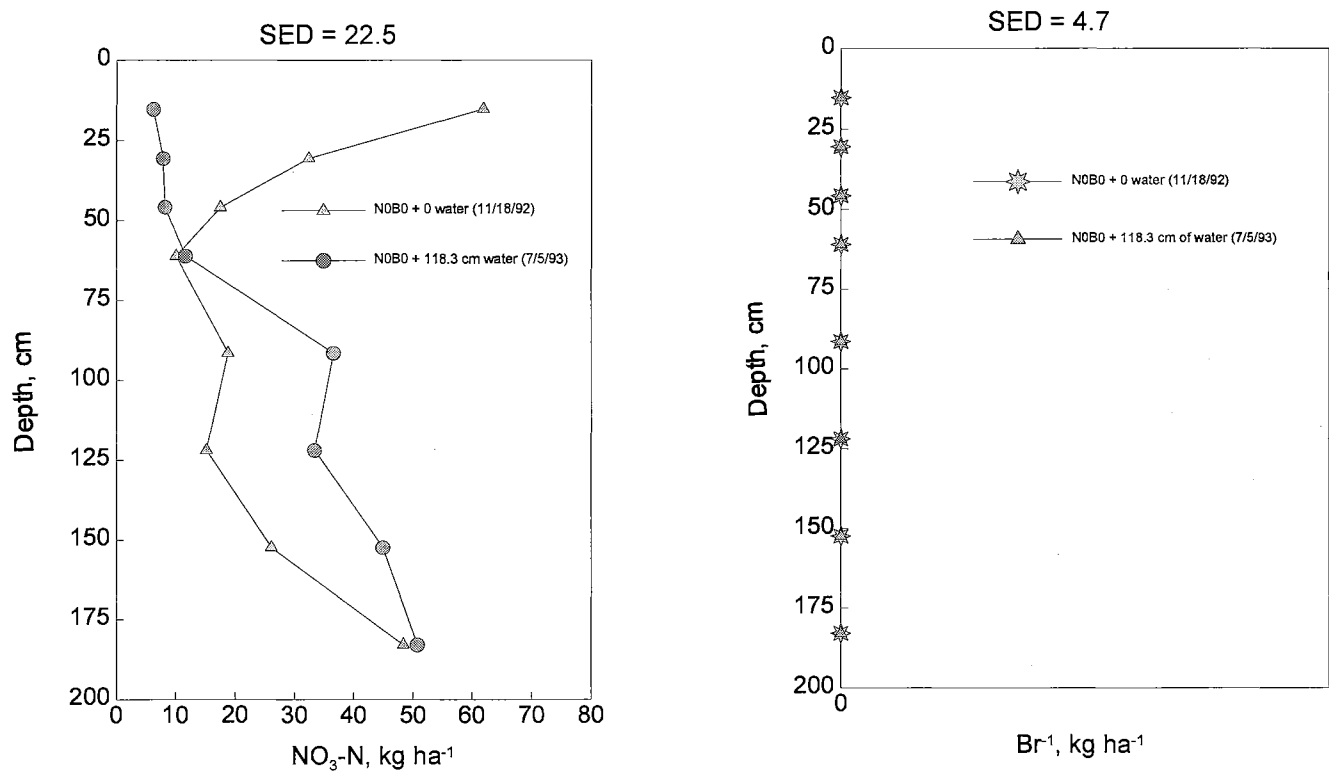


Figure 1. Profile distribution of NO₃-N and Br⁻ for check plots, 0 and 216 days after treatments were applied (N0B0 - 0 kg Br and NO₃ ha⁻¹ as KBr and KNO₃ respectively, treatments 11 (11/18/92) and 12 (7/5/93)), Perkins.

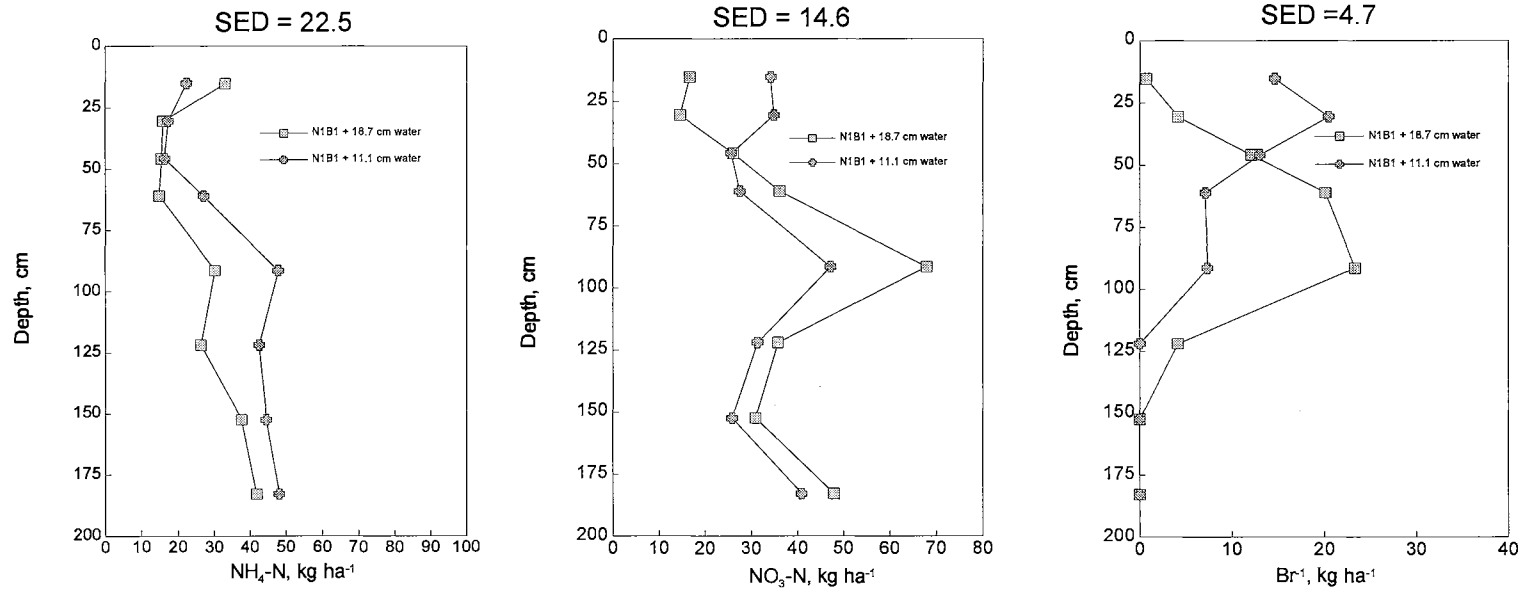


Figure 2. Profile distribution of $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and Br^{-15} , 15 days after treatments were applied, December 3, 1992, Perkins, OK, (N1B1 - 80 kg Br and NO_3 ha^{-1} as KBr and KNO_3 , respectively, treatments 1 and 2).

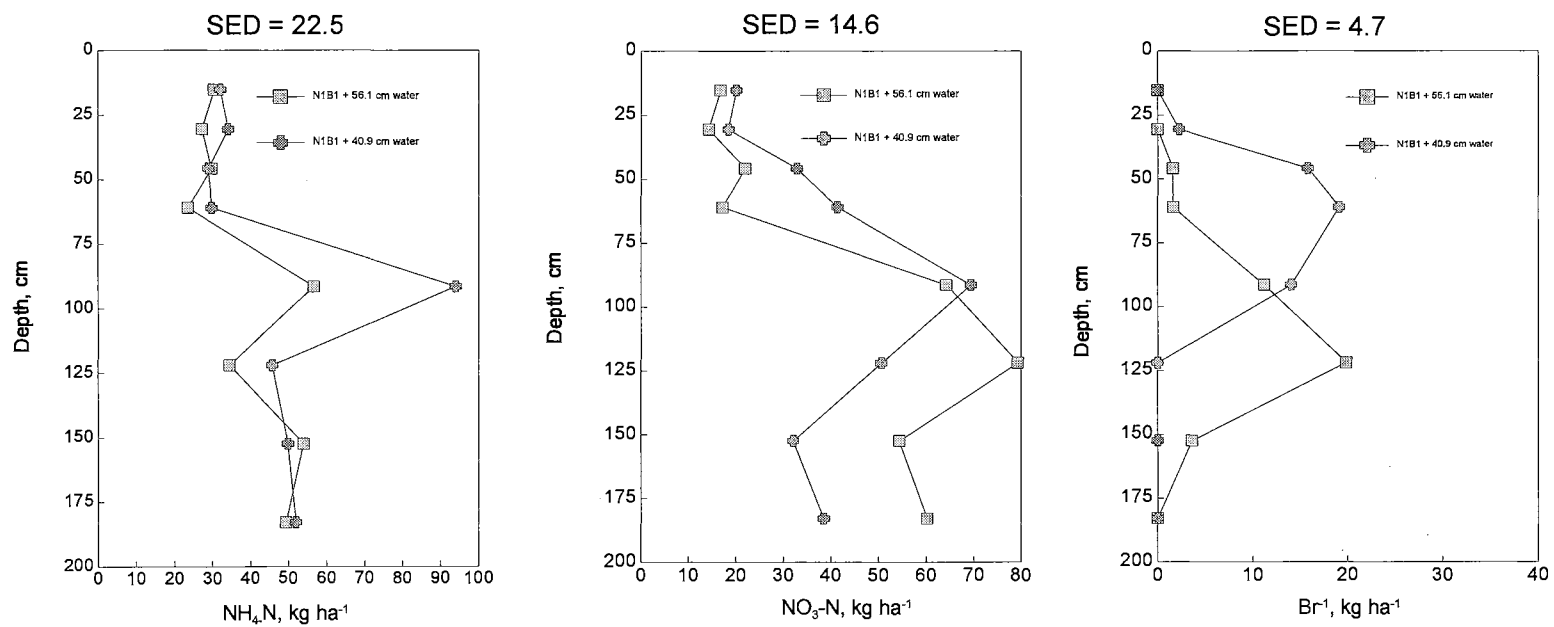


Figure 3. Profile distribution of $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and Br^- , 70 days after treatments were applied, January 28, 1993, Perkins, OK (N1B1 - 80 kg Br and NO_3 ha^{-1} as KBr and KNO_3 respectively, treatments 3 and 4).

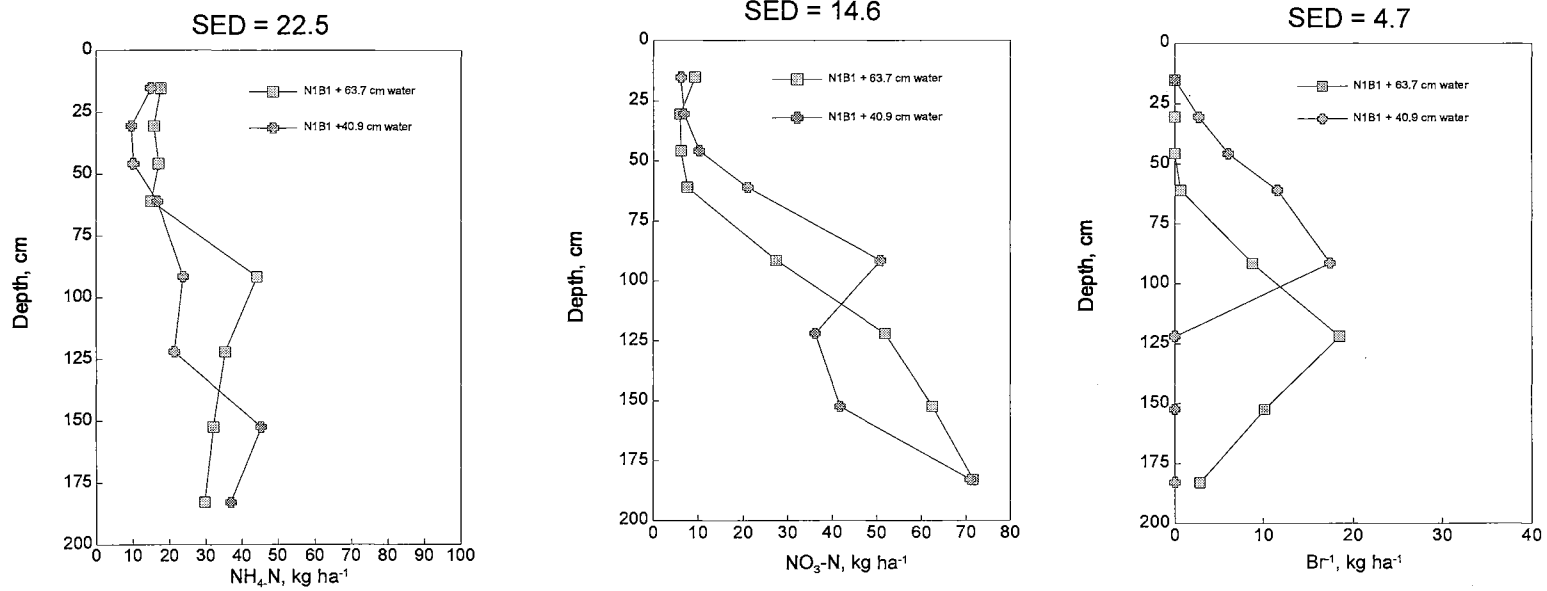


Figure 4. Profile distribution of $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and Br^{-105} , 105 days after treatments were applied, March 3, 1993 Perkins OK, (N1B1 - 80 kg Br^{-105} and NO_3 ha^{-1} as KBr and KNO_3 , respectively, treatments 5 and 6).

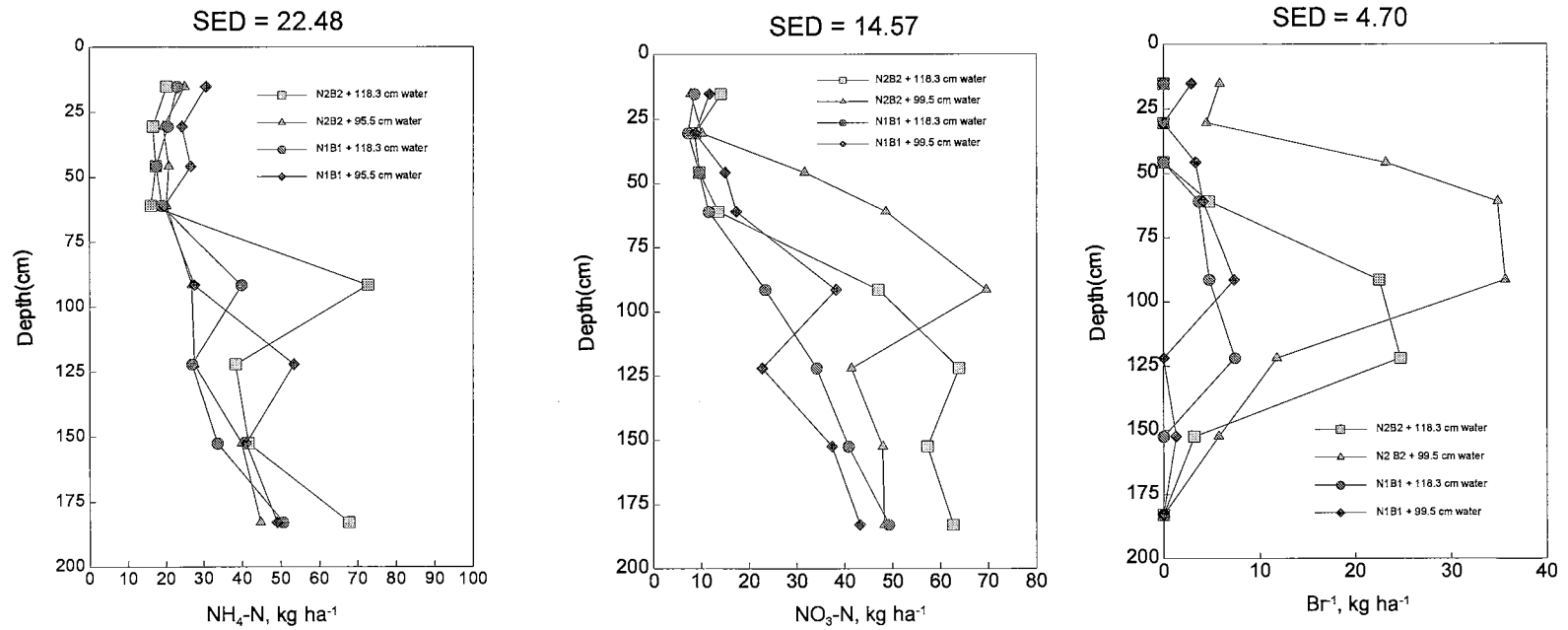


Figure 5. Profile distribution of $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and Br^- , 262 days after treatments were applied, July 5, 1993, Perkins, OK, (N1B1 - 80 kg Br^- and $\text{NO}_3\text{-N}$ ha^{-1} as KBr and KNO_3 , respectively, treatments 7, 8, 9 and 10), (N2B2 - 200 kg Br^- and $\text{NO}_3\text{-N}$ ha^{-1} as KBr and KNO_3 , respectively, treatments 7, 8, 9 and 10).

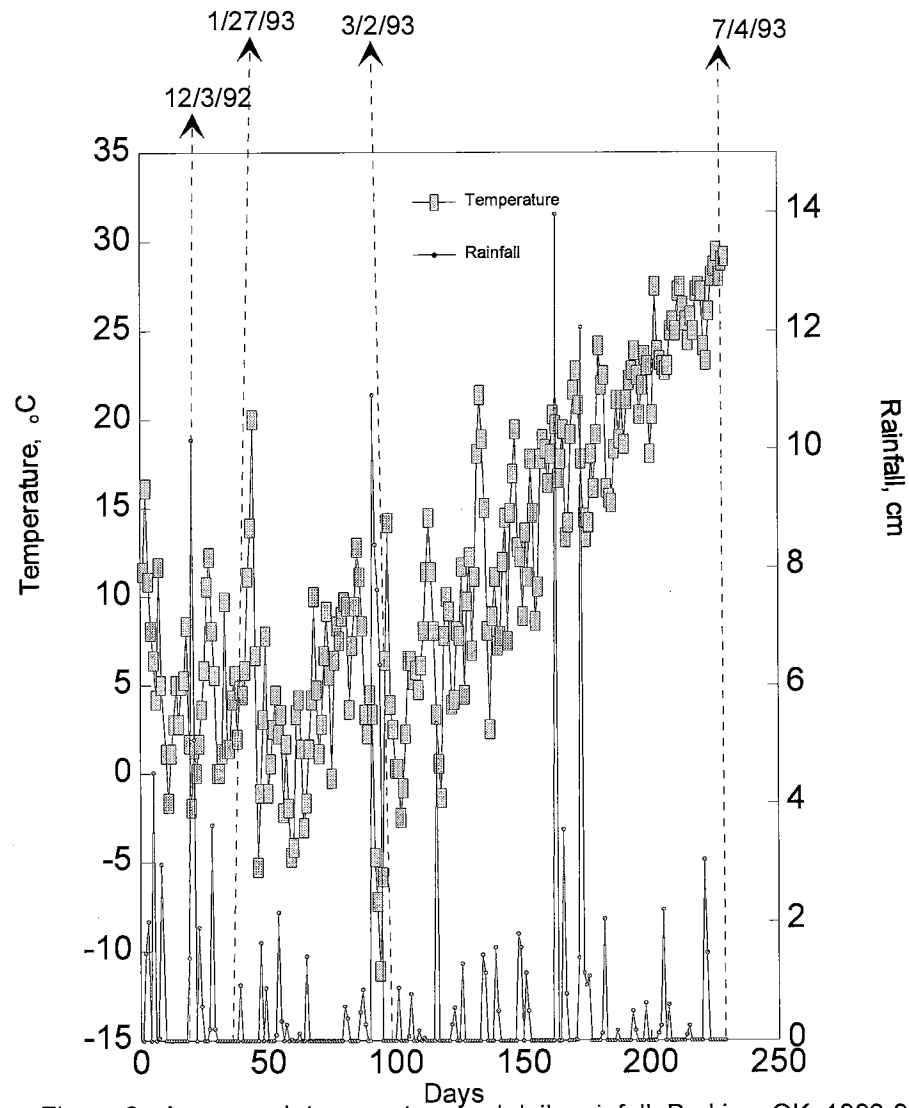


Figure 6. Average air temperature and daily rainfall, Perkins, OK, 1992-93.

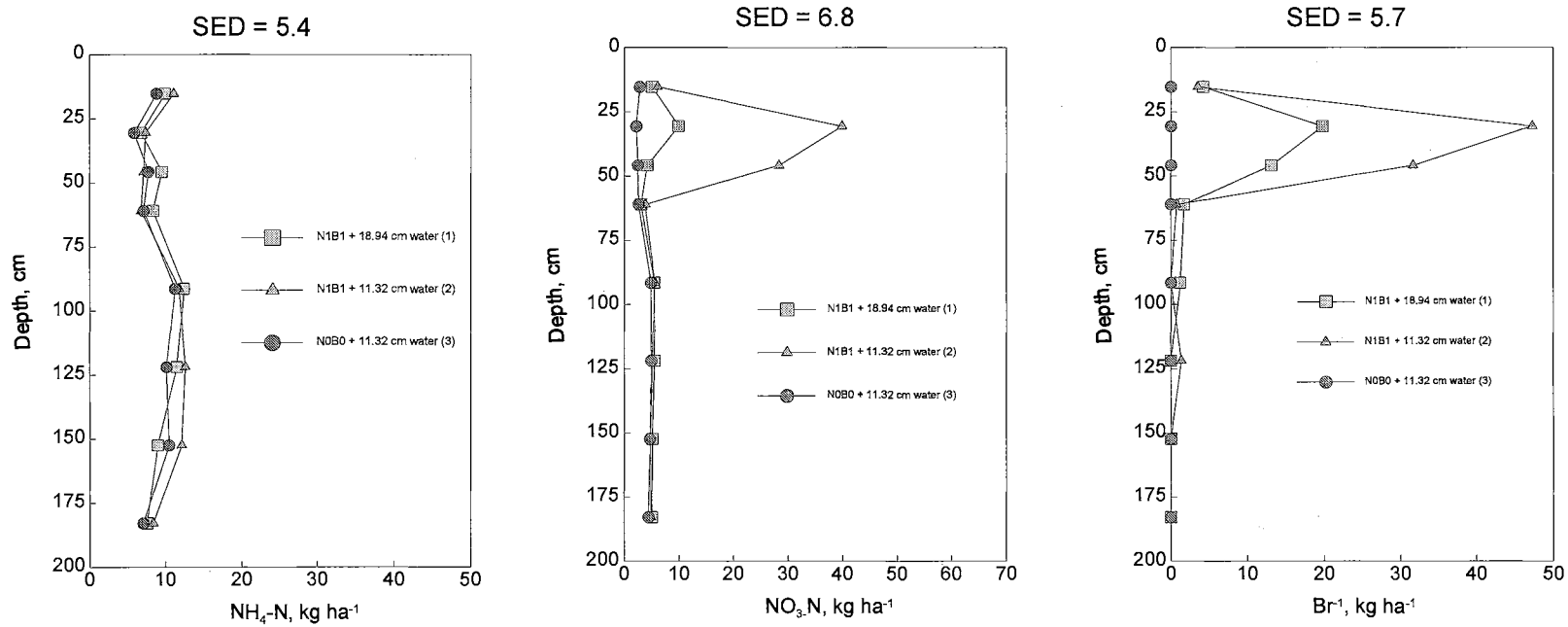


Figure 7. Profile distribution of $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and Br , 26 days after treatment were applied, May 10, 1994, Lahoma, OK (N1B1 - 80 kg Br and $\text{NO}_3 \text{ ha}^{-1}$ as KBr and KNO_3 , respectively) (N0B0, check plot).

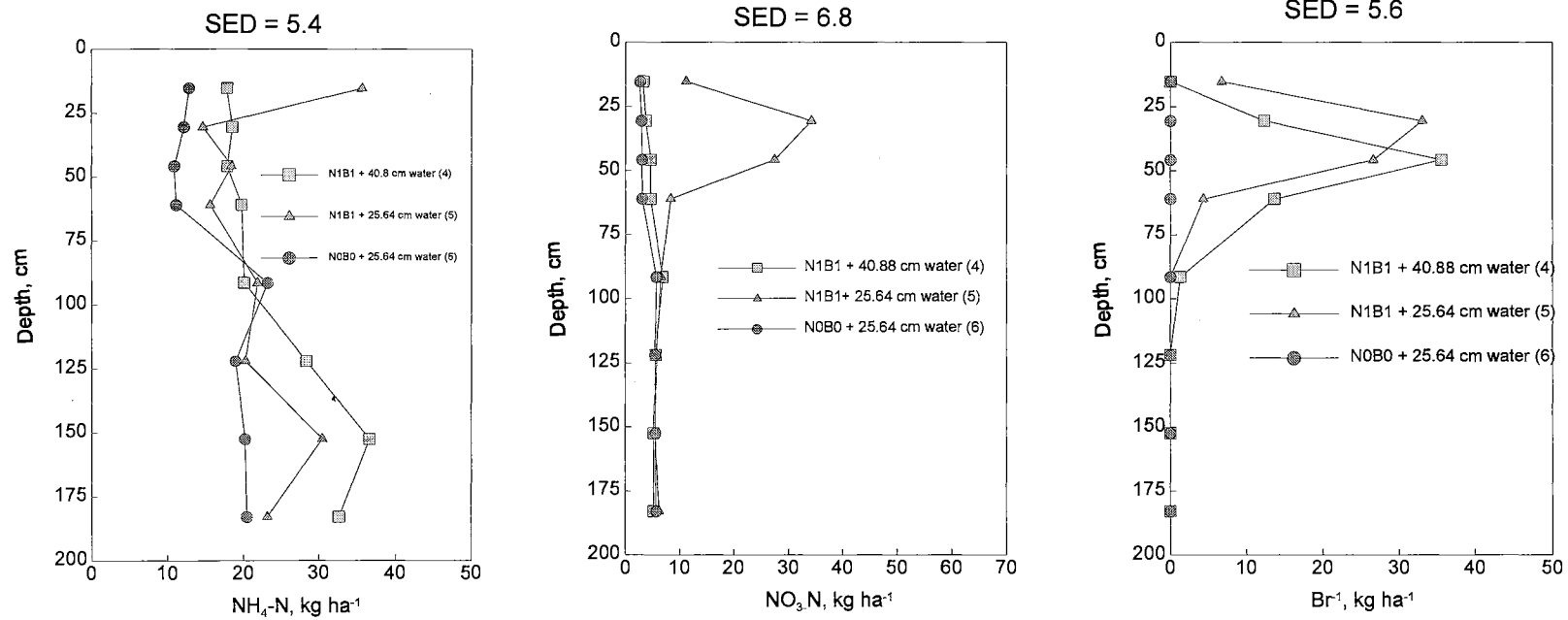


Figure 8. Profile distribution of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ and Br , 46 days after treatment were applied, June 1, 1994, Lahoma, OK (N1B1 - 80 kg Br and NO_3 ha^{-1} as KBr and KNO_3 , respectively) (N0B0, check plot).

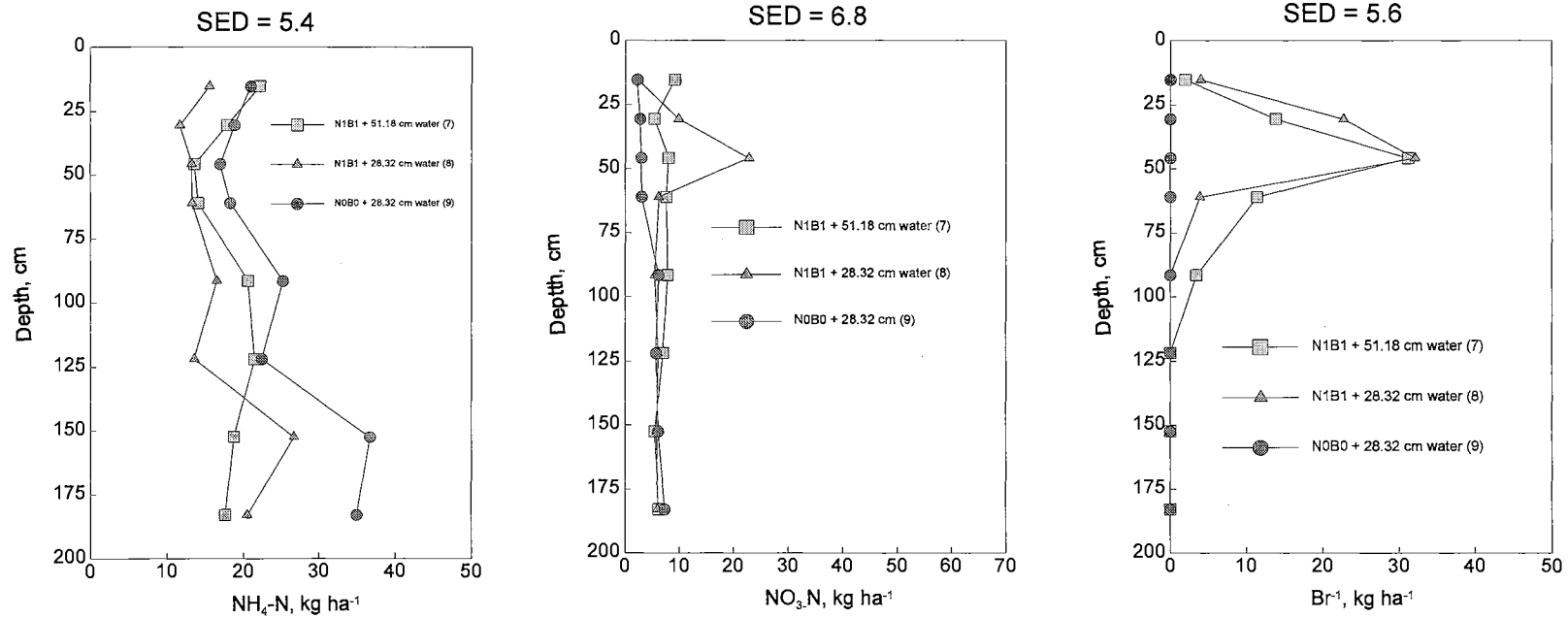


Figure 9. Profile distribution of $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ and Br , 61 days after treatments were applied, June 15, 1994, Lahoma, OK (N1B1 - 80 kg Br and $\text{NO}_3 \text{ ha}^{-1}$ as KBr and KNO_3 respectively) (N0B0, check plot)

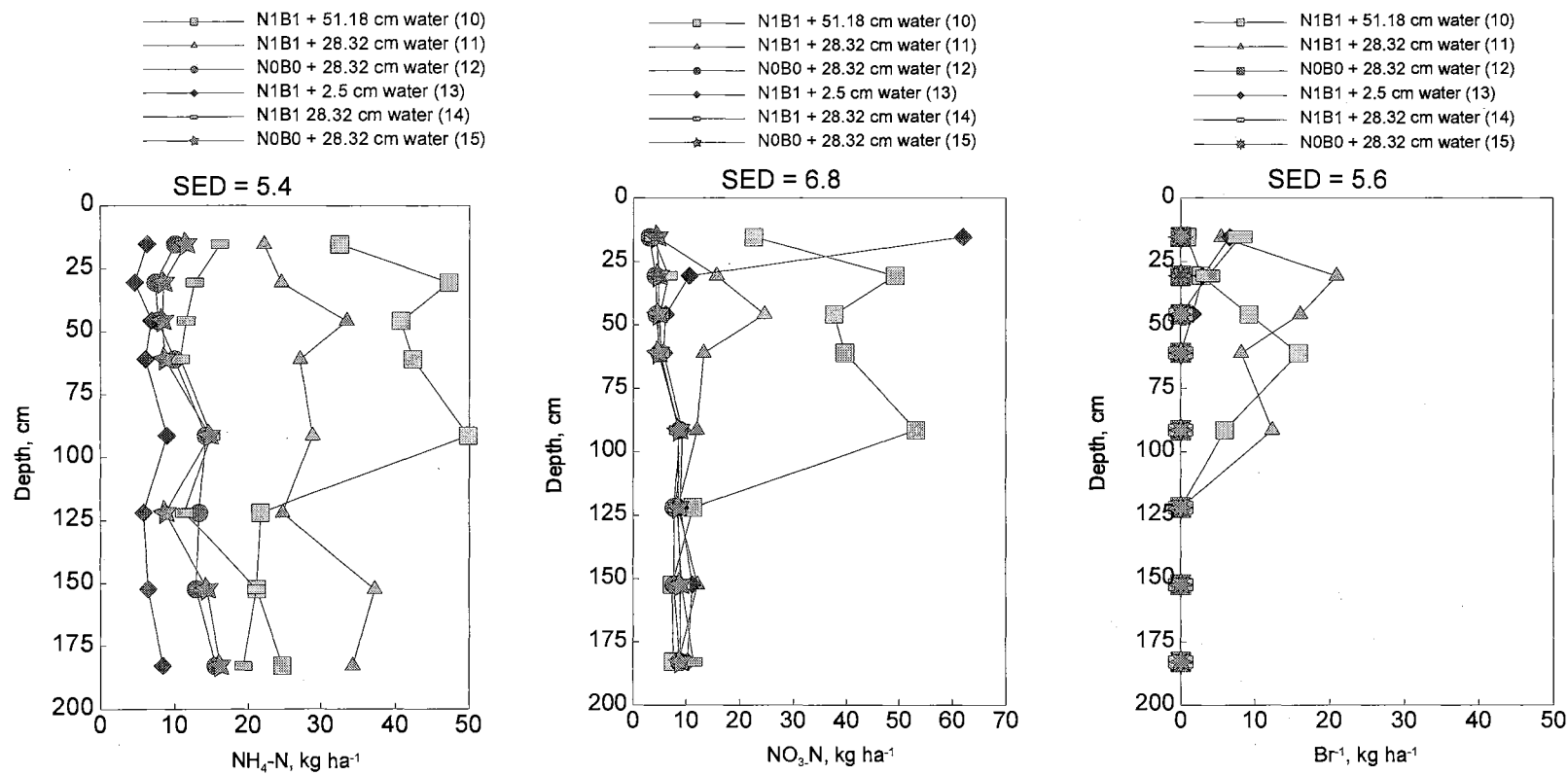


Figure 10. Profile distribution of NH₄-N, NO₃-N and Br, 74 days after treatment were applied, June 29, 1994, Lahoma, OK (N1B1 - 80 kg Br and NO₃ ha⁻¹ as KBr and KNO₃, respectively), (N0B0, check plot).

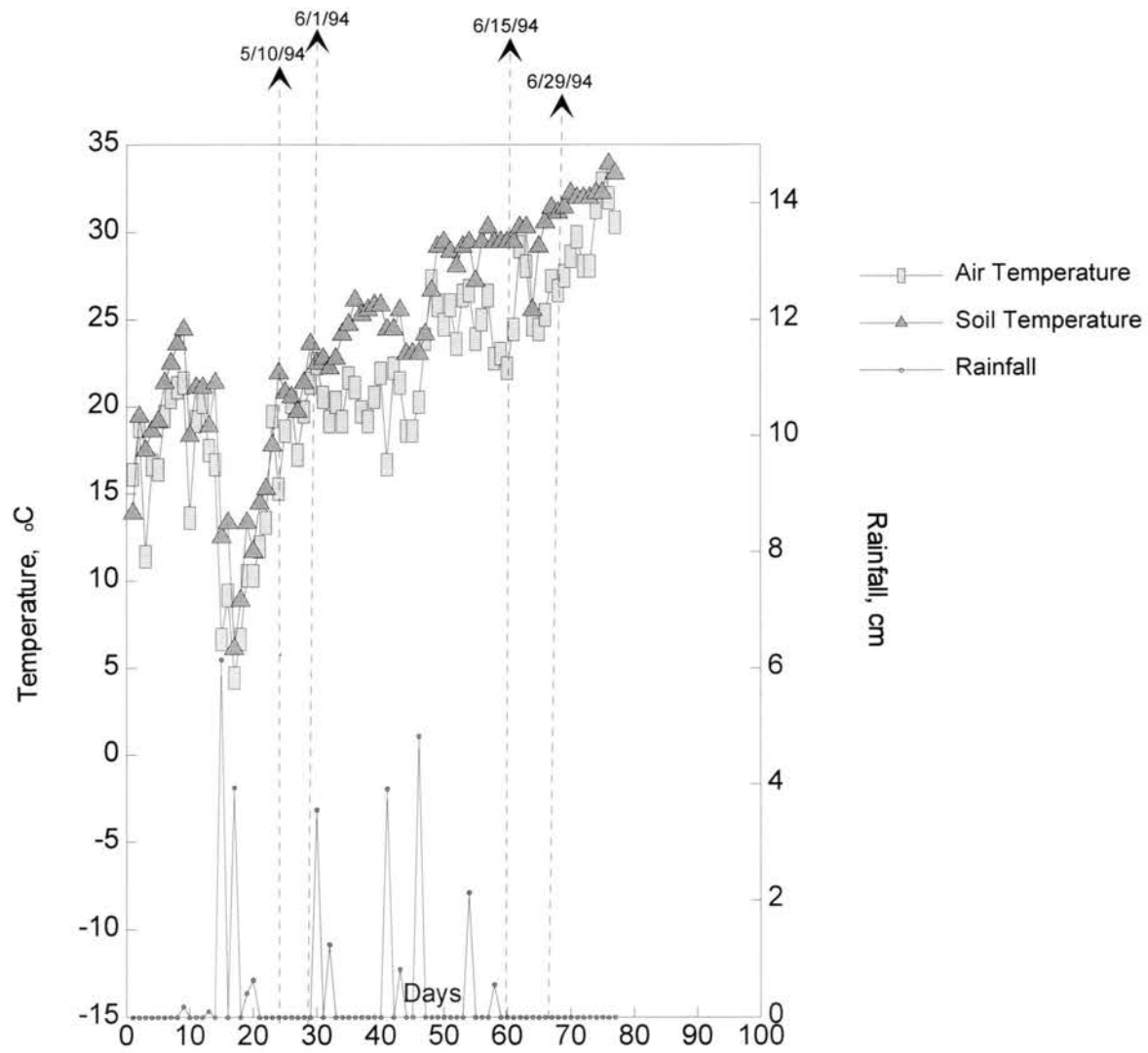


Figure 11. Average air temperature and soil temperature and daily rainfall, Lahoma, OK, 1994

APPENDIX A
MATERIAL RELATED TO
CHAPTER II

APPENDIX A

PROBLEMS ASSOCIATED WITH USING BROMIDE TRACERS IN FIELD EXPERIMENTS

INTRODUCTION

The study of chemical movement (like herbicides, nitrate derived from fertilizer and other solutes that may leach through the root zone) in agricultural soils has used tracers in order to follow the path and potential displacement of the chemical under study. In this regard halides like chloride and bromide have been employed because they are somewhat soluble in water and tend to be leached in the soil profile. However, chloride has a widespread occurrence in soils, rocks, fertilizers, precipitation and other sources (Smith and Davis, 1974), Therefore, the use of bromide (vs chloride) as a tracer has increased. Bromide content of mineral soils average about 6 mg ha^{-1} (range from 0.3 to 40 mg kg^{-1} of Br^{-1}) and in peats average about 30 mg kg^{-1} (range of 12 to 70 mg kg^{-1} of Br^{-1}) (Adriano and Doner, 1982). In general the natural occurrence of bromide is considered low and is also not toxic to plants (Smith and Davis, 1974), since plant uptake is low. While studying the influence of plant uptake on the performance of a bromide tracer, Kung, (1990), found that potato plants absorbed at least 53% of the total applied bromide ions and recovery of bromide

in four soil profiles studied was as low as 11%. It is known that an interaction like this will strongly affect the pulse of the bromide break through curve. While studying bromide movement through the soil it is not rare to find a discrepancy between mass balance values detected and values expected according to rates of applied bromide. Few reports have been published concerning possible interactions of bromide with either organic or inorganic components in the soil. Low recoveries are often explained in terms of physical properties of the soil, water applied, inappropriate sampling, and water evaporation from the soil. Wehtje et al. (1984) studied atrazine leaching on an alluvial loamy sand soil with low organic matter in addition to bromide recovery which this study found to be 84 %. Starr and Glotfelty (1990) studied atrazine and bromide movement through a silt loam soil and found that less than 50% of the applied water, Br, and atrazine could be found. They attributed this to possible processes like one-dimensional movement through the soil profile and rapid downward movement through macropores. Recent studies have identified the formation of halogenated compounds produced by the chlorination of humic acids in the presence of bromide (Peters et al., 1994). Results from this study indicate that due to the high reactivity of chlorine, it reacts rapidly with many natural organic and inorganic compounds, mainly humic materials present in well water. However, the amount and type of products formed is influenced not only by the organic content of the water source, but also by the presence of inorganic compounds like bromide that can favor the formation of brominated compounds.

The oxidation of bromide by hypochlorite has been studied since the beginning of this century, while later studies have indicated that the oxidation of bromide by hypochlorite in the pH range of 10 to 13 (at a various temperatures) is a second-order reaction in which bromide is oxidized to hypobromite (Farkas et al., 1949). The same authors indicated that at lower pH values a series of further reactions take place, in which the hypochlorite and hypobromite are oxidized to bromate and chlorate. Brady and Humiston (1986), mentioned that all the hypohalites (OCl^- , OBr^- , OI^-) have a tendency to disproportionate or enter into a redox reaction with themselves when dissolved in water and to form the corresponding halides (X^-) and halates (ClO_3^- , BrO_3^- , IO_3^-). The equilibrium constants for these reactions are large for all three of these halogens but rates are different. The disproportionation reaction of OI^- , is very rapid at all temperatures, while OBr^- reacts moderately fast at room temperature, OCl^- disproportionation is very slow. Therefore, bromide recovery can be significantly altered when used as a tracer in the soil since it can react with other elements in the soil or in the water. As a result a short term 2 -phase study is proposed to identify bromide products in two soils from different sites and different characteristics and where bromide recovery from previous experimental applications has been variable and unpredictable

MATERIALS AND METHODS

Two phases are proposed for this short term study, the first one will be a modification of the experiment discussed by Peters et al. (1994) for the chlorination/bromination of aqueous humic acid. The second one will use two different soils coming from samples of check plots where experiments that used bromide tracer were done.

First Phase: Chlorination/bromination of aqueous humic acid

Four hundred mg of humic acid will be dissolved in 500 ml. of 0.02N NaOH solution and stirred overnight. This solution will then be neutralized with hydrochloric acid and after that filtered through glass fiber. The resultant solution will be combined with 200 ml of 1.0 M phosphate buffer (pH 7). Subsequently, a 0.05 M NaBr solution will be added to obtain bromide to chlorine ratios of 0, 0.05 and 0.10 and the total volume will be adjusted to approximately 900 ml with deionized water. This step will be repeated three times in order to obtain replications of each one of the solutions with the bromine/chlorine ratios mentioned above. A calculated amount of chlorine, as 0.5 M NaOCl solution will be added to constitute Cl_2/C molar ratios of 0.5 and 2.0 respectively. Lastly, final volume will be adjusted to 1000 ml with deionized water and bottles will be stored in the dark for a period of 16h. Destruction of excess chlorine by the

addition of solid sodium arsenite will be omitted. Solutions obtained in this manner will be saturated with sodium chloride and acidified to pH 0.5 with concentrated sulfuric acid. The final mixture will be extracted three times with 100 ml of glass distilled diethyl ether. The extracts thus combined with the ether will be stored overnight at -20°C in order to freeze remaining water and then concentrated to a 5 ml in a Kuderna-Danish device. Residues obtained will be dissolved in 10 ml of ethyl acetate and taken for GC-MS analysis. The experimental design will be a completely randomized design with 3 treatments, Br/Cl ratios of 0, 0.05 and 0.10 (pH 7 with chlorine to carbon molar ratios of 0.5 and 2.0) and 3 replications. The null hypothesis, H_0 , to be tested is the no formation of brominated and mixed bromo-chloro compounds, and the alternative hypothesis not H_0 .

Second Phase: Chlorination/bromination of soils

For the second phase of this study the same method utilized for the chlorination/bromination of aqueous humic acid will be used, using a sample of 2 grams of soil instead of 400-mg of humic acid, while remaining steps will stay the same. The experiment in this case will have twice the number of experimental units since two soils are to be used (3 Br/Cl ratios x 3 replications x 2 soils). The null hypothesis to be tested will be to find if the formation of brominated and mixed bromo-chloro compounds are found and the alternative hypothesis will be

not H_0 . The soils to be studied are : Soil 1. A soil from the OSU Agricultural Experimental Station of Perkins which is a Teller sandy loam, (fine loamy, mixed, thermic Udic Argiustoll) and Soil 2. A soil from the OSU North Central Agricultural Experimental Station of Lahoma, a Grant silt loam (fine, mixed thermic Udic Argiustoll).

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VITA

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Thesis: SEQUENTIAL MEASUREMENTS OF SOIL $\text{NH}_4\text{-N}$ AND $\text{NO}_3\text{-N}$ FROM TWO-LONG TERM FERTILITY EXPERIMENTS WITH VARIABLE N RATES, AND DISTRIBUTION OF SOIL PROFILE $\text{NO}_3\text{-N}$ UNDER FLOODED CONDITIONS USING A BROMIDE TRACER

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